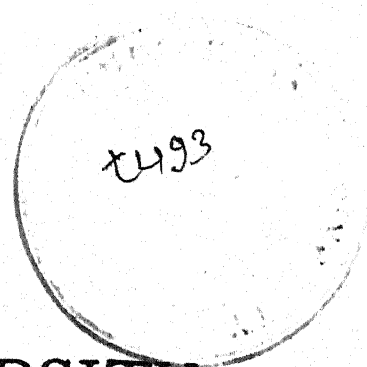


STUDIES ON SOME NEW THREE COMPONENT ION EXCHANGE CRYSTALS

THESIS

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I certify that shri **Naresh Sahgal**, a candidate for the degree of Doctor of Philosophy in Physics of Bundelkhand University, Jhansi has worked under my supervision for a period of more than 200 days as required by the University regulations. The accompanying thesis **"STUDIES ON SOME NEW THREE COMPONENT ION EXCHANGE CRYSTALS** which he is submitting is his genuine work.

I further certify that to the best of my knowledge no much work as been carried out in the same manner or form.

The approach is entirely new and hitherto untouched by any worker in the field.

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CHAPTER - O N E

INTRODUCTION

1.1 General

Ion Exchange Chromatography is a phenomenon that finds many applications in widely divergent fields as agriculture biology, medicine, chemistry and now in physics also. Although the knowledge of ion exchange dates back to the middle of the nineteenth century. Recently interest has been shown by the scientists in this subject other than the fields of soil and water purification.

The early ion exchangers were largely inorganic in origin but subsequently organic exchangers dominated the inorganic exchangers. Organic exchangers have good mechanical and chemical stability.

In recent years again the interest in inorganic exchangers has been revived with the need for high temperature separation in radioactive wastes. To carry out such separations highly selective exchangers are required. These exchangers should not only be stable at higher temperatures but their exchanging power should not be effected by radio active radiators.

Scientists have given deep and serious thought to this topic. They have directed their efforts to get and better products and have achieved success in this direction to a great extent. Synthetic inorganic exchangers have been prepared by modern technology.

Research workers have succeeded in gaining additional

knowledge in their thermal stability, high selectivity for alkali metals. They have also been found useful to perform separation of fission products. Their resistance to radioactive radiations has caused them to be used in the transportation of radioactive substances. Inorganic exchangers have also established themselves useful in the decomposition of nuclear reactor water.

After carrying out researches in the field since a long time, the stage has come when more and better uses of the ion exchangers have to be established. This is also necessary to fulfill the need of scientific provisions of the industrial growth in various fields. To achieve this thought should be given for the preparation of different type of exchangers. Since the properties and hence uses of the compounds depend on their structure. So the prepared exchangers should be studied from their structural point of view also.

Structural studies are of special interest also due to the fact after providing the structure of zeolites it was known that they can be used for the exchange of smaller species only.

Similarly knowing the structure of such compounds it can be possible to explain their properties more effectively.

1.2 Synthetic Inorganic Ion Exchangers

For the last many years ion exchangers have been used to an increasing extent in the laboratory and in plant operations. In natural processes ion exchange occurs in soils, sands, rocks and in living organism.

Nearly two decades back chemists succeeded in

synthesizing ion exchangers which have been found superior to the natural materials.

In 1850 Thompson(1) and Way(2) discovered the technique of base exchange in soils. The materials which are responsible for these phenomena were identified (3,4) as clays, glauconites and zeolites. Clays have ill depwed organic species which possess hydroxyl or carboxyl groups.

Minerals and aluminosilicates have also ion exchange properties. Glauconites are ferrous aluminosilicates analogous to the zeolities as they possess exchangeable potassium ions.

Some coals are natural ion exchangers. They contain carboxylic and other weak acidic groups and can thus be used as cation exchangers.

The first synthetic ion exchanger was prepared in 1903 by Harun and Rumpler(5) synthetic zeolities and permulits were developed by Gaus and other workers for water softening methods(6).

Ion exchangers which occur in nature are crystalline aluminosilicates with cation exchange properties. Zeolities include the mineral analcite $\text{Na}[\text{Si}_2\text{AlO}_6] \cdot \text{H}_2\text{O}$, Chabazite $[\text{CaNa}][\text{Si}_2\text{AlO}_6] \cdot 6\text{H}_2\text{O}$ Harmatone $[\text{K}, \text{Ba}][\text{Si}_5\text{Al}_2\text{O}_4] \cdot 5\text{H}_2\text{O}$, and natrolite are such materials. All these materials have open three dimensional framework with channels and interconnecting cavities in the aluminosilicate lattice other aluminosilicates with cation exchange properties have a lose layer structure for example montamorillovite and bedellite clays. Glauconites which are ferrous aluminosilicates containing exchangeable potassium in their crystal lattice are more dense and rigid so they show very

little swelling hence they are used for the exchange of smaller species.

The first cation exchangers showing similarities with natural zeolites were prepared by precipitation with caustic from acidic solutions of aluminium sulphate and sodium silicate. In recent years various zeolites have been prepared by hydrothermal preparation method which involves crystallization at an elevated temperature from solutions containing silica, alumina and alkali.

Various attempts have been made to synthesize inorganic cation exchangers with other frameworks than aluminosilicate. Fusion permutits have been prepared in which silicon was partly or completely replaced by other tetravalent element such as titanium and tin and aluminium with other trivalent elements such as Fe, Mn, V and P. Many hydrous oxide gets including Fe_2O_3 , Al_2O_3 , Cr_2O_3 , Bi_2O_3 , TiO_2 , ZrO_2 , ThO_2 , SnO_2 , MoO_3 and WO_3 are amphoteric and act as cation exchangers. The oxides of Zr and Sn are most stable.

Recently inorganic cation exchangers with much more satisfactory properties have been prepared by combining group IV oxides with the more acidic oxides of group V and VI. One such important compound is Zirconium phosphate which has been obtained with variable $\text{ZrO}_2:\text{P}_2\text{O}_5$ ratios (7-12). Similar materials can be prepared using arsenic, molybdic and tungstic acids instead of phosphoric acid and Ti, Sn and Th instead of Zr, (9-12). The products are insoluble. These new ion exchangers have high capacities and are superior to the organic resins in their thermal stability and resistance to radiation. Only very few

synthetic inorganic anion exchangers have been made. Gelatinous precipitate of Al and Fe Oxides were used before Organic resins were available. More recently hydrous oxide gels of Zirconium and tin with anion exchange properties have been prepared(12,13).

Just as the applications of the zeolites are limited by their instability in acid solutions so are the organic resins which are limited by their break down in aqueous systems at high temperatures and in presence of ionising radiations. For these reasons attempts have been made to synthesize inorganic exchangers of a variety of types in recent years. They are stable under such conditions. Amongst the well studied synthetic inorganic exchangers, Zirconium phosphate stands out as a unique compound. A survey of studies connected with this exchangers can serve as a pointer to those who are interested in planning newer systems based on this structural network.

1.3A Zirconium Phosphate and Allied Compounds:

A general survey:

Zirconium phosphate (ZrP) has been known over a hundred years but its use as an ion exchanger is of recent origin. The solid precipitates which are commonly called Zirconium phosphates range from amorphous gels to several well defined crystalline compounds.

These were prepared by reaction of soluble phosphate or phosphoric acid with solutions of Zr(IV) salts under a variety of conditions. The compositions and behavior of gels depend upon the conditions of preparation and on some other factors also. After the discovery of Zirconium bis monohydrate(monohydrogen

ortho phosphate) $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ or α -ZrP a variety of crystalline phases have been prepared eg. $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{Zr}(\text{HPO}_4)_2$ or β -ZrP $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ or γ -ZrP, $\text{Zr}(\text{HPO}_4)_2 \cdot 1/2(\text{H}_2\text{O})$ or δ -Zrp, $\text{Zr}(\text{HPO}_4)_2$ or Σ -Zrp, $\text{Zr}(\text{HPO}_4)_2$ or ξ -Zrp, $\text{Zr}(\text{HPO}_4)_2$ μ -ZrP and $\text{Zr}(\text{HPO}_4)_2 \cdot 8\text{H}_2\text{O}$ or θ -ZrP. Though the physical form of ZrP prepared by precipitation varies according to the method employed. But two principal types may be distinguished. A finely divided microcrystalline form in which the ratio of phosphate to Zirconium is approximately 2:1. It is produced by slowly adding the zirconyl nitrate solution and phosphoric acid to a well stirred heated dilute sulphuric acid solution(14). If however, the reagents are mixed rapidly at room temperature rapid precipitation takes place. It gives a gelatinous precipitate (8,15), which settles extremely slowly and which after washing thoroughly gives a gelatinous cake. On drying it shrinks and cracks to give a granular product resembling silica gel. The final product may be opaque and white or glassy and transparent. The above products corresponds to the composition $\text{ZrO}(\text{H}_2\text{PO}_4)_2$. But actually the granular product obtained by rapid precipitation method has phosphate; Zirconium ration less than 2:1 (8,16,17).

When sodium phosphate (Na_3PO_4) is used as a precipitant and ZrOCl_2 in 0.1N HCL is used, the PO_4 :Zr ratio in the product is only 0.69. But with the same zirconium salt if H_3PO_4 is used then this ration is 1.29, though in both cases the reagent composition shows this ratio to be 1.5. Similarly when 6N HCL is used to prepare ZrOCl_2 solution and precipitation is done by phosphoric acid, the ratio is ~ 1.66 but in absence of

hydrochloric acid it can be increased to 1.86 or even ~2.0 by digestion at 60°C with 20% H_3PO_4 and washing finally free from phosphate. Such variation in composition have been shown by Baetsle and Pelsemaekers(16) who worked with 6N acid and Nancollasetal(18) and Larsen et al(19) who worked with lower acid concentrations. Vesely and Pekarek (20) also used 6N HCL but found the presence of chloride ion in the sample which could be removed by washing with water.

Beads of ZrP could be prepared by two types of methods. In the first case the Zirconyl nitrate solution and phosphoric acid are mixed rapidly and sprayed in to a column of mineral oil to get spherical droplet in oil which get out as they reach the aqueous layer at the bottom of the column(21). In the second method(22) the rate precipitation is controlled by complexing zirconium with citrate ion before mixing with phosphoric acid and spraying in to and oil column. Physical and chemical properties of ZrP shows striking physical stability in water even at elevated temperatures.

Particles size distribution measurements after prolonged exposure to water at 300°C show that the material could be used for extended periods at this temperature (21, ref 9 page 17) ZrP is extremely resistant to acids other than HF, H_2SO_4 and Oxalic acid, all of which give zirconium complexes.

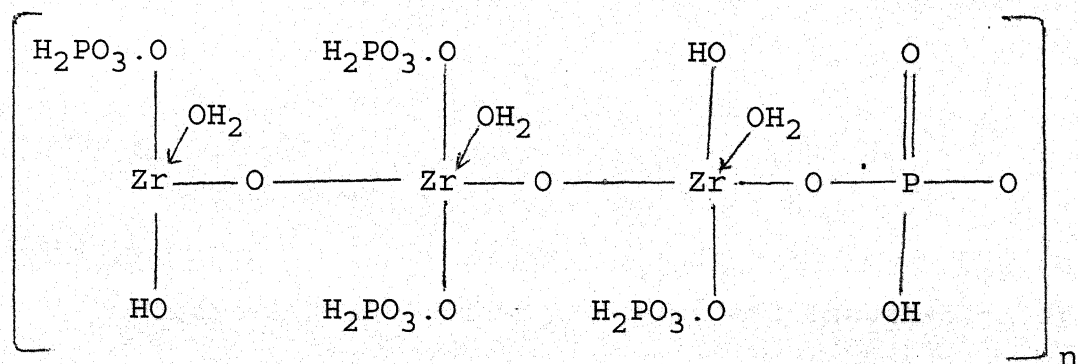
They possess good physical stability both in static and dynamic conditions. The temperature rise up to about 300°C does not affect the stability of the exchanger as far as its ion exchanging properties are concerned. But studies on heating effect of these exchangers have shown structural changes after

about 300°C and the changes continue up to 1000°C. These changes cause decrease in the ion exchange properties of the material as evidenced by the exchange capacity determinations of the heated samples. Though in weakly basic solutions it does show considerable stability, yet in strong bases it dissolves. The exchange capacity shows a distinct rise with pH of the solution from 0.5 meq/g in acid solutions to ~5-5 meq/g in alkaline solutions.

Prolonged washing of the freshly prepared ZrP ($\text{PO}_4;\text{Zr} = 2:1$) does show some hydrolysis of the phosphate at $\text{pH} > 7$ the hydrolysis is quite appreciable and is greater than that of zirconium tungstate or molybdate at pH 7-8. In alkaline solutions, the phosphate is replaced by hydroxyl ion and this phosphate to zirconium ratio may fall down.

The ion exchange properties of ZrP are dependent on the nature of the product prepared and its heating.

Chemical and infra red spectral evidence suggests that ion exchange in ZrP involves replaceable hydrogen atoms in acid phosphate groupings which play a role analogous to that of the sulphonic acid groups of strongly acid organic cation exchange resins.



[Structure of ZrP exchange according to Baetsle and Pelsemekers (16)]

The acidity of the phosphoric acid groups is intermediate between those of the fully ionised sulphonic groups of strong acid organic resins and of the very weakly acid organic resins. Thus ZrP behaves as an efficient cation exchanger in acid solutions. The capacity of ZrP is independent of particle size and depends only on the mass of the material.

The development of ZrP as an ion exchanger stemmed largely from an interest in the separation of metal ions particularly those of the alkali metals under high temperatures and aqueous conditions such as those obtaining in homogeneous aqueous reactor applications.

Although early cation sorption work was concerned largely with the alkali metal encountered in nuclear fuel processing, such as caesium. The extraordinarily high selectivity of ZrP for Cs as compared with the other alkali metal ions is one of the most interesting and useful characteristics of the exchangers. In general these exchangers show high selectivity for alkali and alkaline earth metal ion.

In recent years interest in the inorganic exchangers has been revived with the need for high temperature separations of ionic components in radioactive wastes. In order to make such separations highly selective exchangers are required which are not only stable at high temperatures but which also have the exchange properties unaffected by acidity and high levels of radiation.

Organic ion exchange resins are unsuitable for such applications, as change in selectivity and capacity occur on exposure to radiation and degradation takes place at high

temperatures. More recently ZrP has found potential applications in many other areas. In electrodialysis applications, membranes of ZrP withstand conditions of temperature and pressure, which cause deterioration of their organic components making them attractive for desalination applications and for use in hydrogen oxygen fuel cells.

ZrP or ZrO_2 could be used directly for the removal of ionic impurities from water at the high temperatures characteristic of modulator and coolant circuit in pressurized water reactors ($\sim 300^\circ\text{C}$) has proved a powerful incentive to their study in many countries.

A few parts per billion of Cs can be selectively removed from ordinary sea water or oil well brine. Na and K or Rb and Cs may separated on very short columns with in a matter of a few minutes. Similarly alkali metals can be separated from alkali earths. Among unique properties of these ion exchangers is their ability to exchange effectively in non aqueous solutions and to separate polysaccharides and other compounds which form complexes with tungstate molybdate or phosphate ions in solutions.

Their solubility in strong base has been used in transporting an exchanger containing highly radioactive material by dissolving it in a strong base.

Adsorption and elution of uranium and fission products on ZrP and ammonium molybdophosphate under a variety of conditions have been investigated.

Paper impregnated with ZrP has been used for the rapid chromatographic separations of two and four valent metal ions and of amino acids and alkaloids. The high selectivity of ZrP of

ammonium ions in the presence of Na^+ ions has favoured its use in artificial kidneys. Used in conjunction with urease, Zirconium phosphate has the capability of rapidly removing all the ammonium ions from the hydrolysis or urea dialysed from blood, while enabling the control of other salts in the blood stream.

1.3B Polybasic Acid Salts Other Than Zirconium Phosphates:-

In addition to the zirconium phosphates there exists a large number of other polybasic acid salts which exhibit ion exchange behavior. These include (1) the phosphates and arsenates of titanium, cerium, thorium, uranium, silicon, germanium, tin and lead; (2) the molybdates and tungstates of some of these metals, (3) certain salts of heteropolyacids (4) special preparations including zirconium and titanium, antimonates and (5) some tripolyphosphates.

Both amorphous and crystalline varieties of many of these salts exist.

Some of the important preparations of the above types of inorganic exchangers are summarised below.

Titanium phosphate can be prepared in both crystalline and amorphous forms. In the beginning it was prepared in the form of amorphous gel (11,23). These gels have lower exchange capacity than ZrP gels obtained in the same way. Titanium phosphate gel is highly hydrolysed in acid solutions so their use as exchanger is very limited (24) on refluxing the gels in strong phosphoric acid converts them to a crystalline compound $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ which is found to be isomorphous with α -ZrP.

In Titanium phosphate the exchange of Li^+ and Na^+ ions

takes place at higher pH values in comparison to that of α -ZrP. Thus the cavities must be narrower in α -TiP as compared to α -ZrP.

Zirconium and Titanium Arsenates

Zirconium arsenate gels may be prepared in the same way as those of Zirconium phosphate gels (11, ref 9- paper No 15 p 171).

These gels are converted to crystalline form of ZrAs by refluxing in strong arsenic acid(25,26). The crystals were found isomorphous with those of α -ZrP α -ZrAs crystals show sieving properties similar to that of α -ZrP Rb^+ and Cs^+ ions are not exchanged in acid solutions. They are exchanged only in neutral or alkaline solutions along with the high value of hydrolysis so the ZrAs cavities are nearly of the same size as those of α -ZrP(27). Titanium arsenates both crystalline and amorphous(28) are much more hydrolysed than the corresponding Zirconium arsenates.

Qureshi and Nabi(28) have reported separations of Pb^{++} from Zn^{++} , Mg^{++} , Cu^{++} and Ga^{++} . In all cases some part of the exchanger was soluble.

Cerium (IV) Phosphate -

Cerium phosphate gels were prepared (29, 30, 31, 32) and it was found that the resistance of the gel towards hydrolysis in acid solutions is quite good (30,31).

Methods similar to crystalline zirconium phosphate were employed to prepare crystalline cerium phosphates, The gel was dissolved in conc. H_3PO_4 , then it was diluted until the precipitation occurred and the resultant mixture was boiled to

get crystalline Ce-phosphate. The formula assigned to it is $(\text{Ce-O-Ce}) (\text{HPO}_4)_3 \cdot \text{H}_2\text{O}$ with the compound trace amounts of cations were exchanged. Later on cerium phosphate of a probable formula $\text{Ce}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ was reported, X-ray pattern have shown that it is not isomorphous with $\alpha\text{-ZrP}$ a number of cerium phosphates have been prepared by Clearfield and Herman (33) but the structure determination is still underway. Alberts et al (34) have prepared support-free cerium phosphate sheets from the fibrous, crystalline product with the phosphate-cerium ratio of 2. These sheets were used for several Chromatographic separations. Cerium phosphate has the ability to oxidize the exchanging cation.

Cerium arsenate

Microcrystals of cerium arsenate $\text{Ce}(\text{HAsO}_4) \cdot 2\text{H}_2\text{O}$ were also prepared (35) and the exchange capacity was determined (4.35 meq/g). Exchange of Li^+ and Na^+ by it was observed, while cesium ion was not exchanged. It is resistant to hydrolysis up to pH = 10.

Alberts et al (35) gave a layer structure of the $\alpha\text{-ZrP}$ type to the cerium arsenate.

Thorium phosphate

A fibrous thorium phosphate of composition $\text{ThO}_2 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ has been prepared (36) with the assumption that the compound contains two replaceable hydrogen ions. The exchange capacity was determined experimentally as 3.85 meq/g.

A crystalline $\text{Th}(\text{AsO}_4)_2 \cdot \text{H}_2\text{O}$ was also prepared (37). It was found specific for Lithium ion, so Li^+ ion could be separated from other alkalications by it.

Tin (IV) Phosphate and Arsenate

Stannic phosphate was first prepared in the form of a gel of indefinite composition (38). Its ion exchange behavior was found to be similar to that of ZrP gels. The limiting phosphate tin ration determined was 5:4.

These gels have been examined for the separation of fission products; paper impregnated with tin phosphate have been used for the separation of ions. On heating the gel in 6 to 10 M phosphoric acid crystalline tin phosphate was obtained with the possible formula $\text{Sn}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$. X-ray pattern have shown that it has layered structure similar to α -ZrP. Tin phosphate crystals are strongly hydrolysed in neutral or alkaline pH by all alkali metals cations except Li^+ .

Tin arsenates are quite similar to the corresponding tin phosphates.

Other group (IV) Phosphates

Phosphates of silicon, germanium and lead as well as those of titanium, Zirconium and tin have been prepared by Winkler and Thilo(39). The general formula given to these compounds is $\text{H}_2\text{M}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ except for Si. The ion exchange behaviour of these compounds is very limited as they slowly decompose in aqueous media.

1.4 The Present Work Its Scope and Importance

The brief survey provided in earlier sections on the zirconium phosphate gels of various compositions and structure and also on other allied compounds has given us the impression

that inorganic exchangers are highly selective, resistant to acids and have good thermal stability. There are main features which give them special place over organic synthetic exchangers in ion exchange technology. But at the same time the loss of exchange capacity at elevated temperatures (due to aging or changes in structure) is a basic draw back too. Such exchangers can be improved both in their capacity to exchange ions and stability upto a desired stage with respect to heat treatment. Improvement in the crystalline character of exchanges has been attempted for zirconium phosphate and also zirconium arsenate (25,26) in various ways as to give them better stability even at higher temperatures. Hence attempts in this direction are quite in order.

In recent years Amphlett and Nancollas (40) have tried to obtain an exchanger from strongly complexed zirconium solution with citrate using phosphoric acid. Such a process led them to obtain a highly insoluble product with better exchange properties and special specificities.

Boichinova et al (41) then prepared an exchanger with phthallic anhydride and named it zirconium phthalophosphate. Both these products were better exchangers than ZrP and crystallinity and exchange capacity.

Zirconium arsenate gels may be prepared by precipitation methods similar to those employed for zirconium phosphate gels (42,43) crystals of zirconium arsenate have been found to be similar in structure with α -ZrP.

It is thus natural to think that introduction of extra ionogenic groups to metal arsenate gels can provide improved

varieties of inorganic exchangers. The present work is an attempt¹⁶ in this direction.

The preparation, characterisation and study of ion-exchangers properties of some newer exchangers based on initial zirconium arsenate structure is the basis of the work reported in this thesis.

Introduction of certain carboxylic groups into the network structure of zirconium arsenate can definitely improve the crystallinity of the compounds. Improvement in exchange capacity of the prepared material is also expected. Hence attempts have been made to prepare three new ion exchanging materials from zirconium salts in presence of different types of carboxylic acids. Thus Glutaric, Salicylic and adipic acids have been selected to precipitate zirconium arsenate gels in their presence separately. The acids are dicarboxylic acids out of these the last one is an acid with an additional functional group (OH) in it.

These dicarboxylic acids are expected to provide exchangers of better crystalline properties than simple Zirconium arsenate. Due to the introduction of extrafunctional groups they are also expected to give better exchanging power to the prepared samples. They are thus expected to give polyfunctional inorganic ion exchangers with arsenate and dicarboxylate groups introduced in the Zirconium arsenate structure.

Zirconium shows strong complexing tendencies towards such acids and therefore above expectations are natural. Amphlett et al(40) have also shown citrate ions to be incorporated in the organic material through chemical bonds.

The present work thus includes in its initial chapters the preparation conditions of these new exchangers namely Zirconium Glutero Arsenate (ZrGAs), Zirconium Salicylo Arsenate (ZrSlAs) and Zirconium Adipo Arsenate (ZrAAs).

These exchanges have been prepared from solutions of zirconium ion complexed with the respective acid using sodium arsenate solutions as a precipitant.

The choice of Zirconium as the base element was due to the fact that out of various similar products, zirconium salts have better stability and better ion exchange capacity.

An improvement in ZrAs can give better exchangers and hence this attempt has been made.

The prepared products have been tested further for their stabilities in chemical reagents(as acids and alkalies) and also on heating to higher temperatures. The studies on its exchanging properties under various conditions of electrolyte composition and pH of the solution have also been included in this work. Heat treatment experiments have been carried out to 300-400°C, the temperature encountered in nuclear technology where such exchangers find their application. Exchange capacity changes with temperature and pH from 2-12 have been studied carefully shown this comparative utility as ion exchangers.

Before any new inorganic exchanger is introduced in the field of analytical and industrial chemistry a good deal of fundamental research must be done with it. Each such exchanger is a unique compound with its own properties and behaviour. Hence after confuming the stability and ion exchanging characteristics

of the new ion exchangers prepared. It was thought proper to study some of the fundamental and theoretical aspects of ion exchange using them. Thus equilibria studies involving univalent - univalent exchange have been carried out with all the newly prepared exchangers. The selectivity data for alkali metal ions have been obtained under different conditions of ionic concentrations and loading of the exchanger.

Ion exchange affinity sequences have been found out for these ions with considerations regarding several possibilities.

Rate of exchange is another problem for reaching chemists - who utilize exchangers for various problems and in various fields one must know the correct equilibration time for a new exchanger. Hence attempts also have been made to throw light on this aspect of ion exchange using the new exchangers. Rate studies have been performed with Na^+/H^+ system to get conclusions about complete equilibrations time with the new exchangers ZrGAs, ZrSlAs & ZrAAs.

Swelling characteristics of these exchangers have also been observed in aqueous and non aqueous media.

The data of metal ion distribution between an aqueous electrolyte solution and the exchanger is of great utility in analytical chemistry.

As a matter of fact this is the data which is the ultimate aim of a chemist and which helps him in tackling separation problems. Also the insight into the specificity of an organic exchange can be had from such a data. Hence studies have been performed with the new exchangers to get their distribution

data from equilibrium studies. The distributions data as weight distribution coefficient (K_D) have been obtained for the number of ions with these exchangers. Attempts have been made for the determination of structure of these exchangers.

Infact it is difficult job also. Many have started considering inorganic exchangers as structureless gels. But it is not correct such conclusions are hasty and emerged from the fact that investigators often preparations of a new exchanger at once jump to use them an ion exchange technology and justify the utility of their work. Hence it is desirable to investigate the structural aspect of the prepared polymer(gel).

In the concluding chapter of this thesis attempts have been made to show the presence of carboxylic functional groups carbon hydrogen analysis have also been attempted.

IR spectroscopic results have been used to show the presence and inclusion of carboxylic groups into the network structure of zirconium arsenate polymers.

Attempts at the thermogravimetric analysis of the new exchangers have been very encouraging on the basis of thermo analysis data. Thermograms have been prepared at different stages of decompositions have been marked on the basis of weight loss data.

Thus much support from TG-data has been provided to the final composition results for all the newly prepared materials used as exchangers in the present studies.

The present studies, therefore not only show the preparation of new inorganic ion exchangers. It also shows their utility as materials of great potentiality in the field of ion

exchange technology and analytical chemistry. The much neglected part of structural aspects has also been studied, of course with all the limitations of the laboratory and applicability of the technique available.

This work is expected to be completed in self. Yet it may also provide a guideline to more such studies with different group four metals for preparing newer ion exchangers.

For research work this field is new with a wide scope. Hence it is very essential to utilize it.

As a matter of fact this is the data which is the ultimate aim for doing this type of work. Because it helps in experiments related with separation problems.

Regarding the structure of these gels informations can be gathered by X-rays analysis, IR-spectra and Thermograms obtained from a thermo balance.

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CHAPTER - T W O

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CHAPTER - T W O

Preparations and study of the stability and ion exchange properties of some new ion exchangers.

2.1 Introduction -

Zirconium phosphate was prepared by mixing phosphoric acid to zirconium salt solution, It is an insoluble product. This Compound has been used in the separations of uranium and plutonium from the fission products (1, 2). This compound is stable. even of higher temperatures and is also stable towards many chemical reagents and ionising radiations. Due to these properties of the product it has been used in the processing of cooling water in atomic reactors. This compound has shown its use in changing the frequency of radio waves.

Such properties and uses has proved this compound as a very important ion exchanger.

To improve its properties Amphlett et. al (3) have tried to prepare such compounds in presence of complexing organic carboxylic acids such as citric acid. Similarly Boichinova et al (4) used Pthalic anhydride to prepare zirconium pthalo phosphate from it.

A number of other compounds similar to zirconium phosphate, such as zirconium arsenate, tungstate molybadate have also been obtained.

A short summary such products has been given in chapter I of this thesis.

Some Russian workers (5) have reported similar products these include a chromate compound of 0.6 meg/g capacity between pH 2-10

An oxalate and carbonate have shown weakly acid properties similar to carboxylic type organic resins. A sulphide compound has been found very selective for ions forming insoluble. sulphides.

All the above mentioned studies have been made to improve the capacity and stability of the prepared products.

Attempts made for the introduction of new groups in zirconium based exchangers have given some useful results.

The present attempt to get useful exchangers with improved properties or selectivity trends is thus also an useful attempt.

2.2 The present work

The presence of zirconium in solution has rarely been found in its single tetravalent Zr^{4+} form or even its zirconyl ionic form ZrO^{2+} , even in dilute solution. It is present either in its hydrolysed form such as $ZrOOH^+$ or as a complexed species depending on the nature of the associated anion and water molecules. In concentrated solutions in HCl trimeric and tetrameric species. Such as $[(ZrO)_3(OH)_3]^{3+}$ and $[(ZrO)_4(OH)_4]^{4+}$ have been observed (6,7) Evidences have been provided to show and support the existence of highly charged hydrolysed polymers containing up to three zirconium atoms in each ion. Zirconium oxy chloride has been shown by x-ray scattering studies to be $[Zr_4(OH)_8](H_2O)_{16}Cl_8$ (8) or may have even higher polymer x-ray studies of Ti, Zr & Th compounds have also shown that they give chains of polymers such as $[Zr_4(OH)_6Cr_4O_4]^{8+}$ in zirconium salt solutions containing chromate ion (9). Thus it is quite well known

that zirconium polymers with network of $-O-Zr-O-$ bridges which are cross linked on each alternate zirconium atom are present in such compounds. Such structures contains water molecules or ions with donor atom as coordinated parts to zirconium ion.

It was shown by Amphlett et. al.(3) that when zirconium phosphate is precipitated from complexed zirconium ion it provides exchangers of much better stability & insolubility in the reagents. The qualities add to the utility of the prepared exchanger when such complexing ions have tendencies to give metal chlorates of good stability, then the prepared exchangers can be better in exchanging properties & selectivity to contain specific ions. Thus use of citrate as a complexing ion proved better than simple zirconium phosphate prepared from its oxy chloride or nitrate(3) presence of phthallate(4) similarly proved useful. Depending on these observation, it has been considered here to utilize other media.

Finally the studies for the rates of exchange in an inorganic exchanger are important to get the tune required for completion of the reaction. Such studies are useful in characterising an exchanger for use in different analytical procedures. Even in batch studies for ionic distribution data time complete equilibrium attainment is required. In absence of such a data the equilibrium exchange has to be performed just at randomly. In this chapter therefore the rates of exchange have also been studied wit Na^+ ion at 0.1 N concentration to obtain the times for complete equilibrium attainment for the newly prepared three exchangers. Thus the studies reported in this chapter are ment to prepare and show the utility of the prepared

materials for ion exchanger purposes under different conditions of electrolyte type, pH, temperature and time for equilibrium. Henceforth in this thesis the three products prepared and used as ion exchangers have been referred to as zirconium adipate, zirconium glutarate and zirconium salicylate.

These names have been abbreviated to save space as ZrSlAs, ZrAAS, ZrGAs respectively.

2.3 Experimental

2.3A Reagents and solutions

Zr(IV) salt

Zirconyl nitrate of British Drug House, England was used for the preparation of all the zirconium based exchangers.

Sodium arsenate of Germany was used to prepare aqueous solution of arsenate ions.

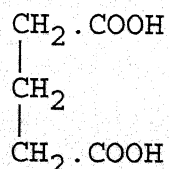
Nitric acid

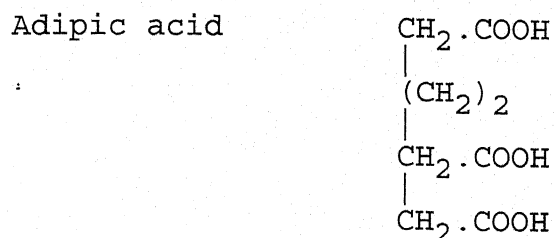
Pure nitric acid (S.D chemicals AR) was used in all preparations; its 1.0 M solution was used in preparing zirconium (IV) salt solutions.

Organic dicarboxylic acids;

Three acids were used in the present studies which were all analytically pure products.

Glutaric acid





*1st 1st 4m NaOH + 100gm NaCl
5 4m NaOH + 50gm NaCl
17 4m NaOH + 100gm NaCl*

For exchange capacity determination electrolyte solutions used were 1.0N Barium chloride and sodium chloride solution of 1, 5 and 10 percents on weight by volume basis. Both salts were BDH, AR reagents, A 0.1 N sodium hydroxide solution was used in total capacity determinations in alkaline medium.

Buffers of different pH values (2 to 8)

Preparation of buffers to maintain values of 2.2, 3.0, 3.6, 4.6, 5.0, 5.6, 6.0, 6.6, 7.0 and 8.0 disodium hydrogen phosphate $12\text{H}_2\text{O}$ solution of .2M strength and citric acid of .1M concentration were used. Twenty ml mixtures were prepared by mixing x ml of disodium hydrogen phosphate and y ml of citric acid solution as per the table below to get buffers of different pH values.

pH	ml of 0.2M $\text{Na}_2\text{HPO}_4(\text{X})$	Ml of 0.1M citric acid
2.2	0.4	19.60
3.0	4.11	15.89
3.6	6.44	13.56
4.6	9.35	10.65
5.0	10.30	9.70
5.6	11.60	8.40
6.6	14.55	5.45
7.0	16.47	3.53
8.0	19.45	0.55

2.3B Preparation of zirconium(IV) salt, organic acid and sodium arsenate solutions

(A) Zirconium(N) salt solution was prepared by taking 7.6 gm of zirconyl nitrate in 5.6 ml of 1.0N nitirc acid. The solution so obtained was more than 0.5H in strength.

(B) Sodium arsenate solutions was prepared by dissolving 22gm of sodium arsenate in to 200 ml of water.

(C) Organic acids were dissolved separately in 2.0 N sodium hydroxide to give solutions of concentrations slightly greater than 1.0M. Thus gluteric acid solution was prepared by dissolving 4.4 gm of acid in 58.0 ml of 2.0N sodium hydroxide for preparing Adibic and salicylic acid solutions similarly 4.9 and 4.5 gm respectively of two compounds were dissolved in the same volume (58 ml) of 2.0 N sodium hydroxide.

All these solutions contained the organic acid in so much quantity that they gave solutions of more than 0.5 strength.

General procedure for preparing the new ion exchanger

Preparation of exchanger with zirconium:organic acid:Arsestate ratio 1:1:1.

The zirconyl nitrate solution in nitric acid (solution A) was first taken in a 400 ml pyrex beaker. A solution of the organic carboxylic acid in sodium hydroxide(solutions C) was added to this with stirring.

This formed a thick while precipitate of the complexed zirconium compound. It was then quickly poured into a 50 ml solutions of sodium arsenate (solution B) taken in another 400 ml beaker provided with a magneticallt driven stirring device. The mixture was stirred vigorously using the magnetic stirrer for

about half an hour. The precipitate so obtained was then filtered and wasted many times with distilled water. The washings were tested for the presence of nitrate ion and washing was continued till the product was free from nitrate ion. The wasted precipitate was then dried in an electric oven at $100^{\circ} \pm 0.1^{\circ}\text{C}$. This provided an amorphous gel type exchanger.

This product after drying was again submerged in water & grounded. It was then filtered and dried again at $100^{\circ} \pm 0.1^{\circ}\text{C}$.

The compound so obtained was in soluble in aqueous solutions and solutions of electrolytes.

2. Preparation of newer ion exchangers with different ratios of organic carboxylic acid with respect to zirconium and arsenate maintained in the ratio of 1:1:1

Preparation procedures similar to the above(1) were followed to get exchangers with 3 more different ratios of organic acid with respect to $\text{Zr}:\text{AsO}_4$ ratios of 1:1

These exchangers were prepared by taking solution C in the above preparations with half, one and half and two times the amounts of organic acids in 58 ml of 2.0N NaOH so as to provide the following ratios for zirconium, organic acid and arsenate as the starting concentrations

- (a) $\text{Zr}:\text{Organic acid}:\text{AsO}_4 = 1:0.5:1$
- (b) $\text{Zr}:\text{Organic acid}:\text{AsO}_4 = 1:1.5:1$
- (c) $\text{Zr}:\text{Organic acid}:\text{AsO}_4 = 1:2.0:1$

2.4 Studies for the chemical stability of the prepared exchangers

The ion exchangers prepared as above were tested first for their stability in acidic and alkaline media. The effect of added mineral acids on the chemical stability of ZrGAs , ZrSlAs

and ZrAAs was studied by taking hydrochloric, nitric and sulphuric acids of different concentrations from 0.1 N to 2.0 N.

2.4(a) Experimental

A known quantity of the prepared material(exchanger) was put in an aqueous solution of the concerned acid taken in sufficient excess. the acid concentration used in such studies included 0.10, 0.25, 0.50, 1.0, 1.5, and 2.0N solutions in distilled water. Always 0.25 gm of the exchanger was treated with 50 ml of the acid solutions and the set was left overnight for any chemical reaction to occur. The supernatant liquid on the next day was analysed for the presence of arsenate ions in all such batches.

Table 2.4.1 summarises the results of such investigations showing the presence or absence of arsenate ion in the treated acid solutions of hydrochloric nitric and sulphuric acids.

Similar studies was performed with alkali solutions also sodium hydroxide and ammonia solutions of 0.1 to 2.0 N concentrations were used to stuffy their effect on chemical stability of the prepared exchangers. Similar batches each containing 0.25 gm exchanger and 50 ml alkali solution were kept over night and were analysed for the released arsenate. Result of these studies have been given in table 2.4.2. The supervalent liquid was also examined for the presence of zirconium ion in both cases zirconium did not appear in acid solutions upto 1.0N. Similarly these effects were seen after boiling the solution also, but no additional effects were observed.

Table 2.4.1

Chemical stability of the prepared exchangers in acidic medium

Acid	Concen- trations	Stability Observations		
		ZrGAs	ZrSlAs	ZrAAs
HCl	0.10 N	No arsenate	No arsenate	No arsenate
HCl	0.25 N	No arsenate	No arsenate	No arsenate
HCl	0.50 N	No arsenate	No arsenate	No arsenate
HCl	1.00 N	Small traces of arsenate	Small traces or arsenate	Small traces of arsenate
HCl	1.50 N	traces of arsenate	traces of arsenate	traces of arsenate
HCl	2.00 N	traces of arsenate	traces of arsenate	traces of arsenate
HNO ₃	1.00 N	No arsenate	No arsenate	No arsenate
HNO ₃	0.25 N	No arsenate	No arsenate	No arsenate
HNO ₃	0.50 N	No arsenate	No arsenate	No arsenate
HNO ₃	1.00 N	Small traces of arsenate	Small traces or arsenate	Small traces of arsenate
HNO ₃	1.50 N	traces of arsenate	traces of arsenate	traces of arsenate
HNO ₃	2.00 N	traces of arsenate	traces of arsenate	traces of arsenate
H ₂ SO ₄	0.10 N	No arsenate	No arsenate	No arsenate
H ₂ SO ₄	0.25 N	No arsenate	No arsenate	No arsenate
H ₂ SO ₄	0.50 N	No arsenate	No arsenate	No arsenate
H ₂ SO ₄	1.00 N	Small traces of arsenate	Small traces or arsenate	Small traces of arsenate
H ₂ SO ₄	1.50 N	traces of arsenate	traces of arsenate	traces of arsenate
H ₂ SO ₄	2.00 N	traces of arsenate	traces of arsenate	traces of arsenate

Table - 2.4.2

Chemical stability of the prepared exchangers in alkaline medium

Alkali	Concentration	Stability Observations		
		ZrGAs	ZrSlAs	ZrAAs
NaOH	0.10 N	No effect	No effect	No effect
NaOH	0.25 N	Yellow colour	Yellow colour	Yellow colour
NaOH	0.50 N	Yellow colour	Yellow colour	Yellow colour
NaOH	1.00 N	Yellow ppt	Yellow ppt	Yellow ppt
NaOH	1.50 N	Yellow ppt	Yellow ppt	Yellow ppt
NaOH	2.00N	Yellow ppt	Yellow ppt	Yellow ppt
NH ₄ OH	0.10 N	No effect	No effect	No effect
NH ₄ OH	0.25 N	Light Yellow colour	Light Yellow colour	Light Yellow colour
NH ₄ OH	0.50 N	Yellow colour	Yellow colour	Yellow colour
NH ₄ OH	1.00 N	Yellow ppt	Yellow ppt	Yellow ppt
NH ₄ OH	1.50 N	Yellow ppt	Yellow ppt	Yellow ppt
NH ₄ OH	2.00N	Yellow ppt	Yellow ppt	Yellow ppt

2.4(c) General Observations and Conclusions

The general observation from these results was that acid solutions of 0.1N, 0.25, 0.5N did not effect the prepared exchangers. But 1.0, 1.5 and 2.0 N acid solutions released traces of arsenate ions in the solution. These traces were sufficient to give faint yellow colorations with ammonium molybdate reagent test. No substantial precipitate of ammonium arseno-molybdic acid was obtained in any of these cases. Thus it appeared that the prepared exchangers were quite stable in acid solutions upto 0.5N, while in acid solutions upto 2.0N little decomposition was observed. Probably the anions associated with the acids displaced some of the arsenate ions at these high acidities (or pH).

In alkali and ammonia solution though 0.1 N solutions did not effect the exchangers but 0.25 N to 1.0 N solutions elerted arsenate ions. This increased with increase in the alkali concentration so much so that good amount of yellow precipitate was obtained at 1.0 alkali solutions.

Hence the general conclusions that could be derived from such studies are

- (i) The prepared exchangers are very stable in acid solutions up to 0.5 N concentrations.
- (ii) They are stable in alkali solutions only up to 0.1 N
- (iii) General chemical stability of these is much more in acids than in alkali
- (iv) No decomposition of the exchangers tool place with respect to zirconium ion up to 1.0 N acidity

2.5 Studies on the effect of heat on the physical appearance of the prepared materials

It is said that the heated zirconium based gels work better as exchangers and their solubility in electrolytes decreases for the heated samples. Heating during preparations provides the product some what crystalline forum and heating of the prepared gel afterwards gives it a stable granular appearance. Does heating decomposes the product substantially or is it tolerable up to a certain extent? This is the questions which is of prime importance for the inorganic exchangers. The studies reported in this section gives only the results of outward changes in the products newly prepared so that physical stability of the products due to heating can be checked. A section later on has been assigned to test the effect of heat on exchange capacities of the new exchangers.

2.5(a) Experimental

The compounds prepared as shown in sec. 2.3 were first dried at room temperature $\sim 25^{\circ}\text{C}$. The lumps so obtained were disintegrated in distilled water and again dried at $\sim 25^{\circ}$. Such samples of ZrGAs, ZrSlAs and ZrAAs were subjected to heat treatment in carefully regulated electric ovens.

Each time a small amount of the product (dried at $\sim 25^{\circ}$) was taken in a watch glass and kept in the oven controlled for a fixed temperature ($\pm 1^{\circ}\text{C}$). The observations were made after heating the samples for about 4 hours. Any change in their physical appearance was noted.

In this way the effect of heat on all the newly prepared materials were observed. The temperatures up to 300°

were taken with a difference of 50°C while later on differences were increased considerably

2.5(b) Results

The table below (table 2.5.1) gives the colour changes of the products at different temperatures which are indicative of the physical state and expected decomposition and stability of the products.

Table - 2.5.1

Effect of heat on the chemical characteristics of the prepared exchangers

Temperature °C	ZrGAs colour, crystalline state		ZrSlAs colour, crystalline state		ZrAAs colour, crystalline state	
25°	white	amorphous	white	amorphous	light grey	amorphous
50°	white	amorphous	white	amorphous	light grey	amorphous
75°	white	amorphous	white	amorphous	light grey	amorphous
100°	white	partly granular	white	partly granular	light grey	partly granular
150°	white	partly granular	white	partly granular	dark brown	partly granular
200°	white	partly granular	light brown	partly granular	black	partly granular
250°	white	partly granular	light brown	partly granular	black	mixed particles of different forms
300°	light yellow	mixed particles of different forms	brown	mixed particles of different forms	Dark brown	mixed particles of different forms
400°	yello-wish black	mixed particles of different forms	brown	mixed particles of different forms	dark brown	mixed particles of different forms
1000°	white	crystalline	white	crystalline	white	crystalline

2.5(C) General Conditions

The conclusions that can be drawn from the results are as follows

- (i) The temperature range from 25° - 100° does not effect the physical stabbility of any of the four exchangers.
- (ii) At 200° ZrAAs shows some sign of decomposition.
- (iii) At 200° ZrSlAs also shows some sign of decomposition
- (iv) All tend to decompose partially from 300° onwards and become white at 1000° suggesting similarity of forum at 1000°
- (v) Changes in colour from 300° onwards are indicative of the decomposition of the organic part which breaks down complebidity as the temperature approaches above $\sim 500^{\circ}$

2.6 Studies for the ion exchange capacities of the newly prepared exchangers

2.6(a) To prove the ion exchanging capabilities of newly prepared exchangers it is customary to determine their exchange capacities under different conditions.

The property which characterises a chemical compound or a polymer as an exchanger is the number of groups that it possess to bring about the exchange reaction. This property can be measured experimentally as milliequivalents of exchangeable ions per gm of the dry ploymer (or exchanger). One can also determine these groups by their ionisation studies in solution as weakly or highly dissocited acids (or bases).

The determination of total exchange capacity is not so simple as it appears. It depends on several factors. These include

- (a) The low rates of exchange
- (b) Unfavorable exchange equilibria between certain pairs of ions
- (c) Inaccessibility of certain exchange sites and
- (d) Instability of some exchange polymers. Equilibrium pH titrations help in getting the information regarding the exchanging groups in the resin/or a polymer.

These titrations need setting up of experiments with sample of the exchanger in contact with varying amounts of the ions to be exchanged. Attainment of equilibrium may require any time and the titrations for the generated hydrogen from a cation exchanger can be made with KOH solutions noting the pH of the solution simultaneously. Thus pH titration curves can be obtained to get the information about the ionisable groups present in the exchanger. But such titrations are useful only when the exchanger has functional groups of highly ionised nature. For others the complete equilibrium is either not attained or several weeks may be needed to cover up the expected range of the pH. Hence, these methods are not convenient for all types of exchangers including weakly acidic resinous products from arsenate containing polymers.

The method involving a large excess of a solution containing an ion exchangeable for the ion in the resin is much better and quicker for this work. The ion in the exchanger is thus made to get exchanged and come into the solution completely. This is determined then experimentally by titration. This procedure has been modified to suit the requirement of newer types of resins and wider applicability (15,16).

Thus we can measure under equilibrium conditions the exchange of a counter ion for the ion in the resin taking an excess electrolyte. The method provides the limiting exchange capacity for the exchanger. But for total exchange capacity a dynamic exchange process is more useful (refer to Kunin ref. pg 34 etc.) using the hydrogen form of the exchanger and using the exchangeable ions (as NaCl) in presence of sodium hydroxide. The presence of sodium chloride helps in driving out the hydrogen ion of the weakly acidic resins completely. The concentration of sodium chloride influences this removal and hence for all routine work a 5% NaCl solution is preferred with 0.1 N sodium hydroxide in sufficient excess. The hydrogen ion titrated in the exchange reaction comes in the electrolyte solution neutralising the corresponding equivalent quantity of the alkali. The estimation of the alkali after the process gives the alkali neutralized by the liberated hydrogen ion. From this milli equivalents of the exchangeable H^+ ions can be calculated.

2.6(b) The Present Work

In this present work the three newly prepared exchangers have been used to determine their exchange capacities under different conditions and by different methods. Thus first of all the limiting capacities have been determined in neutral medium (or using neutral salt solutions) using barium chloride¹⁷ and sodium chloride as electrolyte solutions.

Later on the total exchange capacity method of Kumin¹⁸ has been adopted to find out capacity in acidic solutions i.e. at pH values lower than 7.0.

To see the effect of pH on capacity similar methods have been used to determine the exchange capacities of all exchangers in solutions of pH values from 6.6 to 12.

The effect of the salt concentration has also been seen at pH values 10-11 to get the maximum possible exchange values for these exchangers.

2.6.c Experimental

The exchange capacities were determined by following the procedures given below:

I Procedures for determining the limiting exchange capacities of the prepared exchangers

Exactly 0.25 gm of the exchangers was used to determine this capacity under equilibrium conditions. Well-stoppered flasks of 150 ml capacity were used to keep exactly 50 ml normal barium chloride solution in it. The required amount (0.25 gm) of the exchanger was then added to each such flask. The solutions were then given swirling motion to bring the said and solution phases well in contact. These batches were left as such for 24 hours. However, they were shaken intermittently to help the attainment of equilibrium quickly. After this aliquots were with drawn from each flask (availing exchanger particles) and estimated for the acid generated due to exchange. This estimation was done by titrating the aliquots with 0.01 N sodium hydroxide solution.

Similar batch studies for limiting exchange capacity were carried out with normal sodium chloride also. The results of these as milli equivalents of hydrogen ion per gm of the dry

resin (17) have been given in table 2.6.1.

II Procedure for determining total exchange capacity of the polymers in alkaline solution (method of Kunin, 17).

One gram of the exchanger was taken in an Erlenmeyer flask (cap. 500 ml.). An electrolyte solution containing 5% sodium chloride and sodium hydroxide sufficient to give its 0.1N solution in deionised water was used for exchange purposes. The solution was standardised properly to check the sodium hydroxide strength in the mixture. Exactly 200 ml of this solution was added to the exchanger kept in the Erlenmeyer flask, the sample was stoppered well, shaken intermittently. It was left as such for 48 hours after which 50 ml aliquots of the supernatant liquid was titerated with standard 0.1 N hydrochloric acid using phenolphthalein as indicator. From such titre values the exchange capacity was calculated by using the formula given below

$$\begin{aligned} \text{Exchange capacity in} \\ \text{milliequivalents/gm H form resin is} = & \frac{(200 \times \text{Normality of NaOH}) - 4(\text{ml of acid} \times \text{normality of acid})}{\text{Sample weight}} \end{aligned}$$

Such studies were performed with all the three exchangers ie ZrGAs, ZrSlAs and ZrAAs.

To see the effect of salt concentration on the exchange capacity, similar studies were performed with each type of exchanger using 1% and 10% sodium chloride in the electrolyte solution containing 0.1N sodium hydroxide. The pH of such solutions was noted by a pH - meter and it was ~11.

These results of total exchange capacities in alkaline medium have been given in table 2.6.2 at different salt

concentrations. The trend of changing salt concentration is clearly given in fig. 2.6.1.

III Procedures for determining by limiting exchange method at different pH values:

To determine exchange capacities of the prepared exchangers at different pH values of the electrolyte solution the following procedure was used.

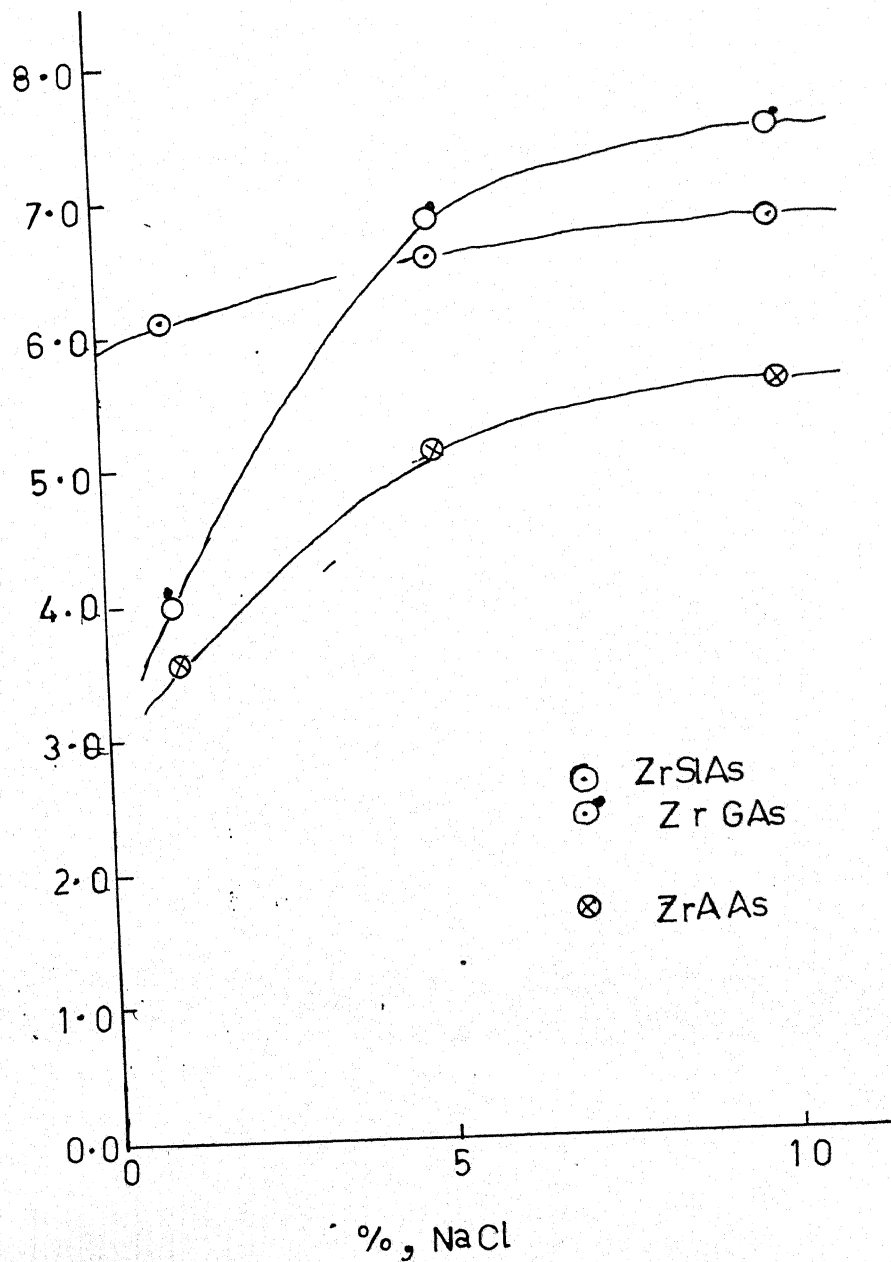
Each time 0.25 gm of the exchanger was equilibrated with 50 ml of the electrolyte solution containing sodium chloride to provide 1.0 N solution and sufficient buffering material to give the correct pH required for the experiment. Thus each time 20 ml of sodium hydrogen phosphate, citric acid buffer (see table for compositions) and 25 ml of 2.0 N sodium chloride with 5 ml distilled water was used to give the 50 ml electrolyte for exchange purposes. Such solutions were equilibrated for ~48 hours with 0.25 gram of each exchanger in separate Erlenmeyer flask (cap. 150 ml.). After equilibration supernatant liquid was analysed for the generated acidity due to exchange of sodium ions in the solution phase.

As the solutions were also acidic initially hence the separate electrolyte samples prepared in the same manner also estimated for their content. The difference in acidity after exchange was taken equivalent to the H^+ generated due to exchange at the pH of the solution.

Such studies were carried out at different pH values from 2.2 to 8.0 to observe effect of pH of the solution on the exchange capacities of the new exchangers.

EFFECT OF SALT CONCENTRATION
ON EXCHANGE CAPACITY
AT PH 10 TO 11

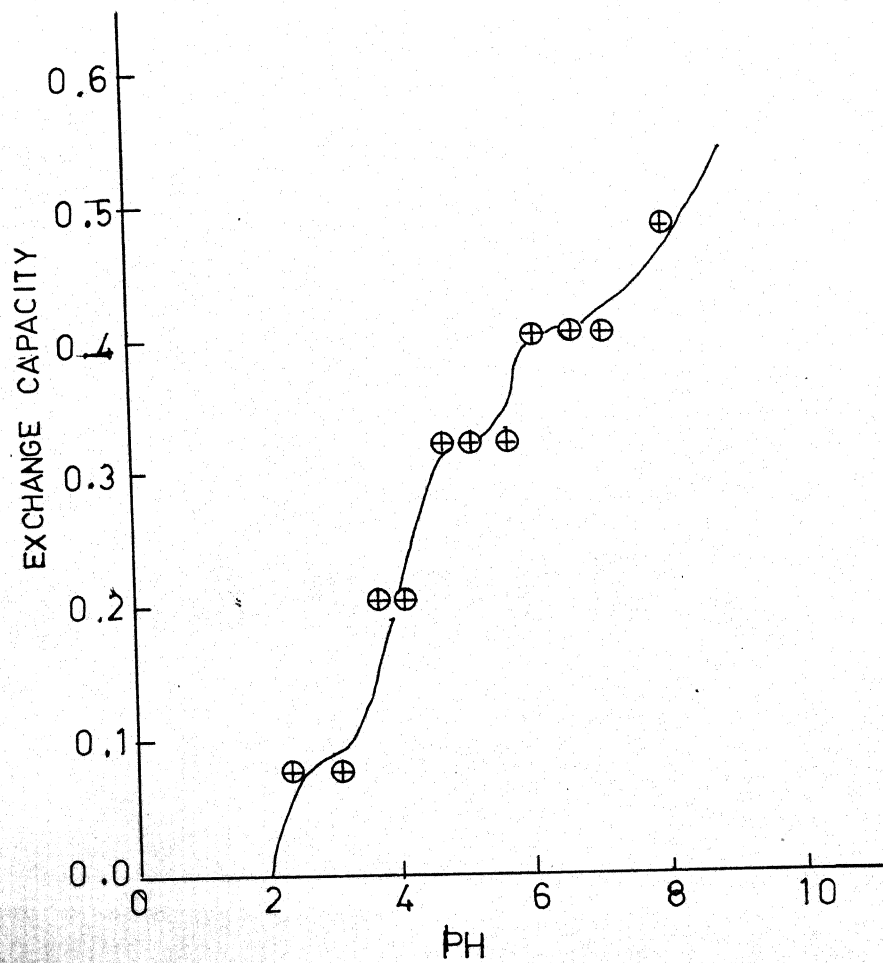
FIG. 26 I



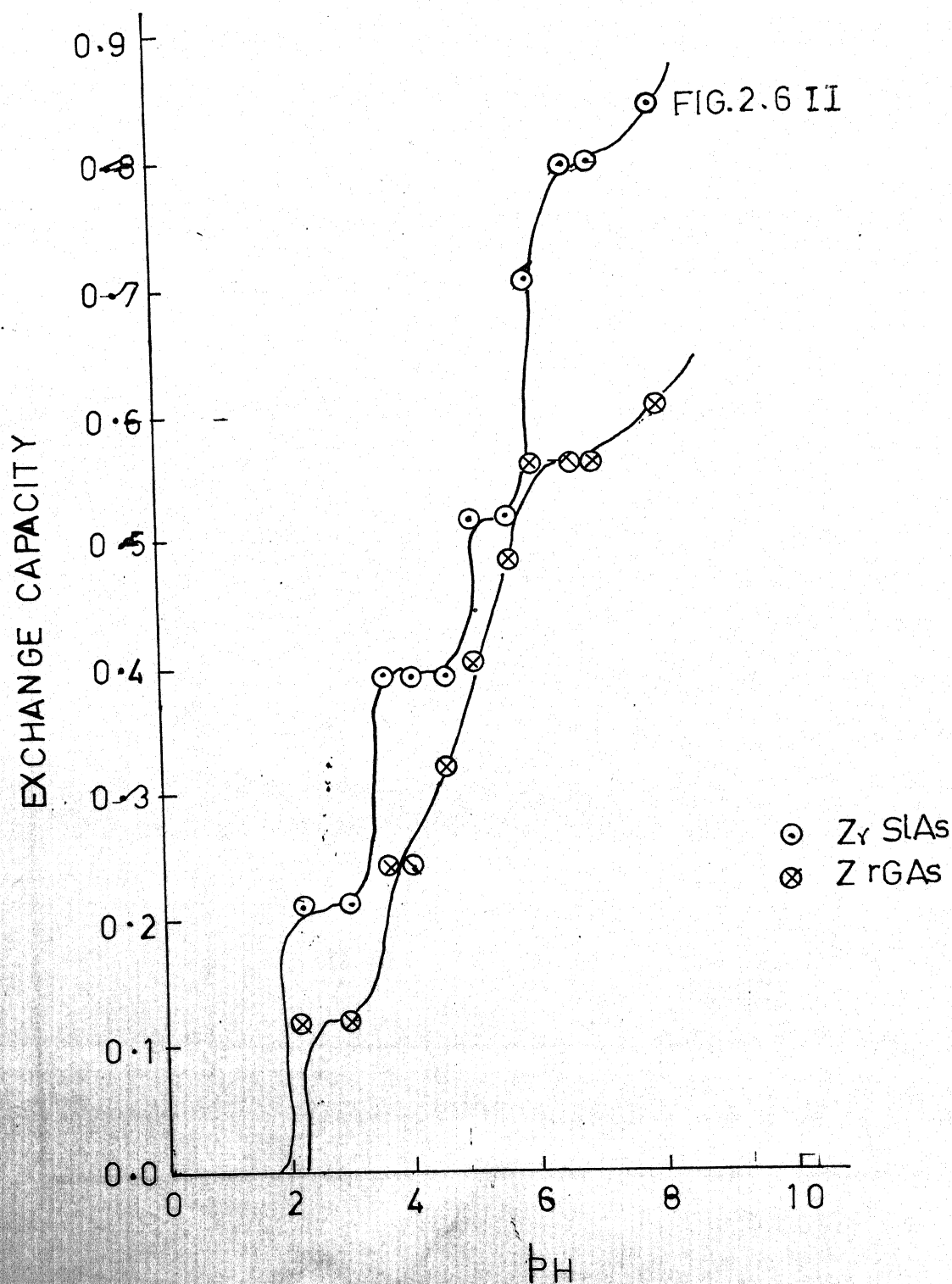
EFFECT OF PH ON THE EXCHANGE CAPACITIES OF DIFFERENT SYNTHETIC EXCHANGERS

FIG. 2.6 II I

⊕ Zr AAS



EFFECT OF PH ON THE EXCHANGE CAPACITIES OF DIFFERENT SYNTHETIC EXCHANGERS



2.6.d

The results

Limiting ex

Medium

Natural
BaCl₂ (N)
solution

Natural
NaCl (N)
solution

Table 2.6.2

Total exchange capacities of synthetic exchangers in alkaline medium

pH	Presence of salt %	Total exchange capacities meq/g in alkaline medium		
		ZrGAs	ZrSlAs	ZrAAs
10 to 11	1%	6.00	3.86	3.60
10 to 11	5%	6.48	6.64	5.04
10 to 11	10%	6.60	7.30	5.524

Table 2.6.3

Effect of pH on the limiting exchange capacities of synthetic exchangers

pH	Salt %	Limiting exchange capacities meq/g		
		ZrGAs	ZrSlAs	ZrAAs
2.2	5%	0.24	0.14	0.08
3.0	5%	0.24	0.14	0.08
3.6	5%	0.38	0.28	0.20
4.0	5%	0.38	0.28	0.20
4.6	5%	0.38	0.40	0.32
5.0	5%	0.58	0.40	0.32
5.6	5%	0.58	0.40	0.32
6.0	5%	0.70	0.46	0.40
6.6	5%	0.79	0.46	0.40
7.0	5%	0.79	0.46	0.40
8.0	5%	0.88	0.54	0.48

in tables 2.6.3. The graphs have also been plotted to show the change in exchange capacity with changing pH of the solution (Fig. 2.6 II and 2.6 III).

(1) The limiting exchange capacities of different exchangers have shown a maximum capacity of ~ 0.78 meq/gm dry exchanger for ZrAAs. The values are lesser for other exchangers in the order $\text{ZrGAs} > \text{ZrSlAs} > \text{ZrAAs}$

(2) Use of an electrolyte of uni and divalent metal ion does not make much differences in the exchange capacities by this method. Hence it is the quantity (concentration and volume) of the electrolyte which should be in excess to the quantity of the exchanger used. The nature of the ion is not very much important, of course it should have affinity lesser than the ion in the exchanger which is to be removed.

(3) The total capacity of inorganic exchangers prepared here show quite high values in presence of sodium hydroxide (ph 10-11). The total capacity is again very high for ZrGAs and ZrSlAs. But it is clear from the data of table 2.6.2 that presence of salt and its concentration is very important for these ion exchangers. When the total capacity of ZrGAs changes from 6.00 meq/gm to 6.6 meq/gm for change of NaCl concentration from 1 to 10%, it is 3.96 meq at 1% NaCl 6.64 meq at 5% NaCl and 7.30 meq at 10% NaCl for ZrSlAs.

Increase in exchange capacity with increase in salt concentration has also been shown in ZrGAs and ZrAAs (see fig 2.6.I)

4. The highest exchange capacities have been observed for these exchangers at pH 10-11 in presence of 10% NaCl. The value for ZrSlAs is highest, 7.30 meq per gram dry resin. It is 6.6 meq for ZrGAs and 5.524 meq for ZrAAs. Thus all the exchangers show values of quite high order in alkaline solutions.

5. The difference in limiting and total capacities of these exchangers show that the ionisable groups of these exchangers are mostly weakly acidic and they show their utility only at high pH of the solution. Capacities due to strongly acidic groups (limiting are quite low for these products.

6. The effect of acidic and alkaline media is clear from exchange capacity data at different pH values (fig. 2.6 II and III).

A gradual increase in capacity with increasing pH is a general conclusion.

2.7 Studies on the effect of heat on the exchange capacities of the exchangers

The uptake of a metal ion by an product prepared is dependent on the temperature of its heating before use. It has been shown for zirconium oxide which shows a marked decrease in capacity with increase in drying temperature. In zirconium arsenate also the changes in structure have been shown from infrared spectra(20) and x-ray studies(3). This was followed by obvious changes in capacity of the exchanger. It is quite clear that not only the conditions of preparation but also the drying temperatures of the prepared product change their properties widely (3). The heating of the sample is required to give it a more crystalline form and to make it more stable towards the electrolyte solutions.

Thus the observations regarding capacity changes with heating of the prepared exchangers are very useful, not only to show their utility limits but also to throw light on the possible structural changes in it. Hence attempts have been made here too

to study the limiting exchange capacities of the prepared three exchangers after heating them to different temperatures. Thus temperatures from 25° to 400° have been used to get exchange capacities after heating to a particular temperature. The earlier studies of sec 2, on the effect of heat on the stability of these compounds have shown that temperatures above 400°C bring about decomposition of the organic part introduced into the zirconium based exchangers. Hence it is no good determining capacities at temperatures above 400° .

Table 2.7.1 gives the results of such studies for limiting exchange capacities studied for these exchangers by using 1.0 N barium chloride solutions. Graphs in figure 2.7.I indicate the trend very well for changing temperature conditions.

Conclusions

The results show a decrease of exchange capacity in all cases after 100°C . The temperatures up to 100° do not alter the exchange capacities of the original compounds up to 150° the change is minor in ZrGAs and ZrSlAs but it is much lowered for ZrA₅. There after the capacity falls quite sharply up to 300° and becomes negligibly small at 400°C . Thus a regular decrease in exchange capacities have been observed in all cases using the heated samples from 100°C to 400° . It also means that $\sim 100^{\circ}$ is the temperature which can be used to get the granular, more stable material for ion exchange purposes.

2.8 Limiting exchange capacities of the exchangers prepared with different Zr; Organic acid; AsO_4 ratios

To see which of the ratios Zr:Organic acid; AsO_4 provide better exchangers, exchange capacities for the products prepared

as per details given in sec. 2.3 have been determined. The values given in table 2.8.1 are the limiting exchange capacities of these various products.

The results indicate that the best exchange capacities are given by the prepared products when the ration Zr; organic acid; AsO_4 were 1:1.0:1 with lesser organic acids, the exchange capacities were quite low; while increase to 1:1.5:1 or 1:2.0:1 ratios for the Zr; organic acid; AsO_4 were of no use. Either the capacities remained the same or decreased slightly (ZrGAs, ZrSlAs, ZrAAs)

Hence the optimum ration found out from these studies for getting a good exchange was 1:1.0:1 or Zr; organic acid; AsO_4 .

2.9 Swelling characteristics of the prepared ion exchangers

Inorganic ion exchnagers behave quite differently from the point of view of their swelling characterstics. Swelling in water is quite pronounced in clay minerals used as exchangers, but in synthetic products from Zr or other groups four elements, the swelling characterstics are quite different. Though the prepared products are hydrated to a great extent but when they are dried they lose much of their water except molecules which are linked to the structure more strongly. Now if they are again put in water, they do not absorb water to the same extent. Though they show swelling in many cases upto 100%, this effect is negligibly small for samples heated to higher temperatures. Zirconium phthallate and zirconium phthalophosphate have been shown to give swelling of about 103 and 116% respectively(7). But in general zirconium phosphate products are denser and do not

swell considerably.

The newly prepared exchangers have also been studied for their swelling characteristics.

2.9(a) Procedure for swelling study

Always a fixed value of the exchanger was filled by tapping in the specially prepared glass cylinders.

The volume was noted carefully. Then the required solvent was added so as to cover the resin completely. It was added in sufficient excess to allow complete swelling for the material. The air bubble were removed by tapping of these cylinders. The cylinders so filled were kept over night for the exchangers to swell completely. After this the volume changes were again read off and noted. Swelling was calculated as percentage change in the volume of the exchanger.

Such studies were carried out with water, and 100% ethanol as pure solvents and 2 mixed solvents with 50 and 25% ethanol solutions in water.

2.9(b) Results:

Results in tables 2.9.1 to 2.9.4 report the data for the 3 exchangers. The comparative data is given in table 2.9.5. Swelling has been shown as a positive change in the tables, while decrease in volume has been shown as a negative change.

2.9(c) Conclusions

(1) the prepared exchangers show very little swelling in water. It is ~1.1 to 2.07 in different cases. This shows quite denser structure of the products.

(2) In absolute ethanol the exchanger contract a bit rather than swelling. This contraction is to the extent 3.75. This has been observed for exchangers lowest being for ZrAnAs.

(3) In mixed alcholic solutions also there is contraction rather than swelling.

(4) The observed effects in alcholic solvents may be due to dehydration of the water of crystallisation or coordinated water present in zirconium based exchangers. These water molecules can be replaced also by donor ethanol molecules.

2.10 Studies on the rates of exchange with the new exchangers

The exchange rates are diffusion controlled and these depend, therefore on the structured characteristics of the exchangers. The swelling also influences the ion diffusion rates in the resin or exchanger matrix.

Resins with better swelling properties make it easy for the ions to diffuse through the resin matrix and bring it to the proper exchange site. Hence with organic synthetic exchangers the rates are generally faster. But with inorganic exchangers of denser structures, it is not so. The rates of diffusion may become slower to cross the resin matrix for reaching the exchange site.

It is also clear from several ion exchange studies in non aqueous solvents that the nature of the solvent alters the diffusional rates considerably. In other words film diffusion of the counter ions is also one of the controlling factors for rates. But if water is the solvent, this factor is much less important.

As the newly prepared exchangers are inorganic in origin, they are in general more dense than the moderately cross linked organic resins. The rates are, thus, expected to be slower in such systems. To know the exact situation, the rates of exchange with Na^+ ions have been studied here with ZrGAs, ZrSlAs and ZrAAs exchangers.

2.10a Procedures

Rate studies have been made by using always 0.5gm of the exchanger and 50 ml of 0.1 N sodium chloride solution in water. The reactants were taken in an erlenmeyer flask of capacity 150 ml. The solutions were stirred in these studies in these studies by using a magnetic stirrer. Right from the beginning ie immediately after adding the exchanger to the electrolyte solution aliquots (1.0 ml) were withdrawn after certain time intervals to estimate the generated acidity in the external electrolyte solution. These aliquots were titrated with suitably standardised 0.01 N sodium hydroxide. Such estimations after proper time intervals were done to cover up a sufficiently long period of about four and half hours. The last reading was obtained after keeping the batches over night.

From the titration data milliequivalents of Na^+ exchanged for H^+ were determined. These values show the rates of change of concentration of the ion in the electrolyte solution. From these the attainment of fractional equilibrium at different time intervals were calculated as Q_t/Q_0 . The values of Q_t indicates the changes of concentration at time t and Q_0 shows this for final equilibrium state.

Plots have been made for these values of Q_t/Q_o against time to evaluate the time for complete equilibrium attained by the exchanger and the electrolyte solution with respect to Na^+/H^+ exchange reaction.

2.10b **Results**

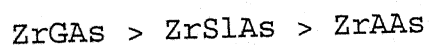
Table 2.10.1 gives the data for rates for the exchange of Na^+ ion with ZrGAs, ZrSlAs and ZrAAs.

Tables 2.10.2 gives the comparative values of time of attaining complete equilibrium for this exchange reaction.

The plots in figures 2.10-I and II show the rate changes visually and show that the rates in these exchangers are comparatively slower.

2.10.c Conclusion

1. Results point out the rates to be slower in these exchangers generally the time periods for attaining complete equilibrium show the rates to be slowest in ZrGAs. The order that shows higher rates is



2. It is essential therefore to equilibrate these exchangers for sufficiently longer period in affinity or distribution studies.

3. To bring out maximum capacity values also these will need equilibration for a longer period.

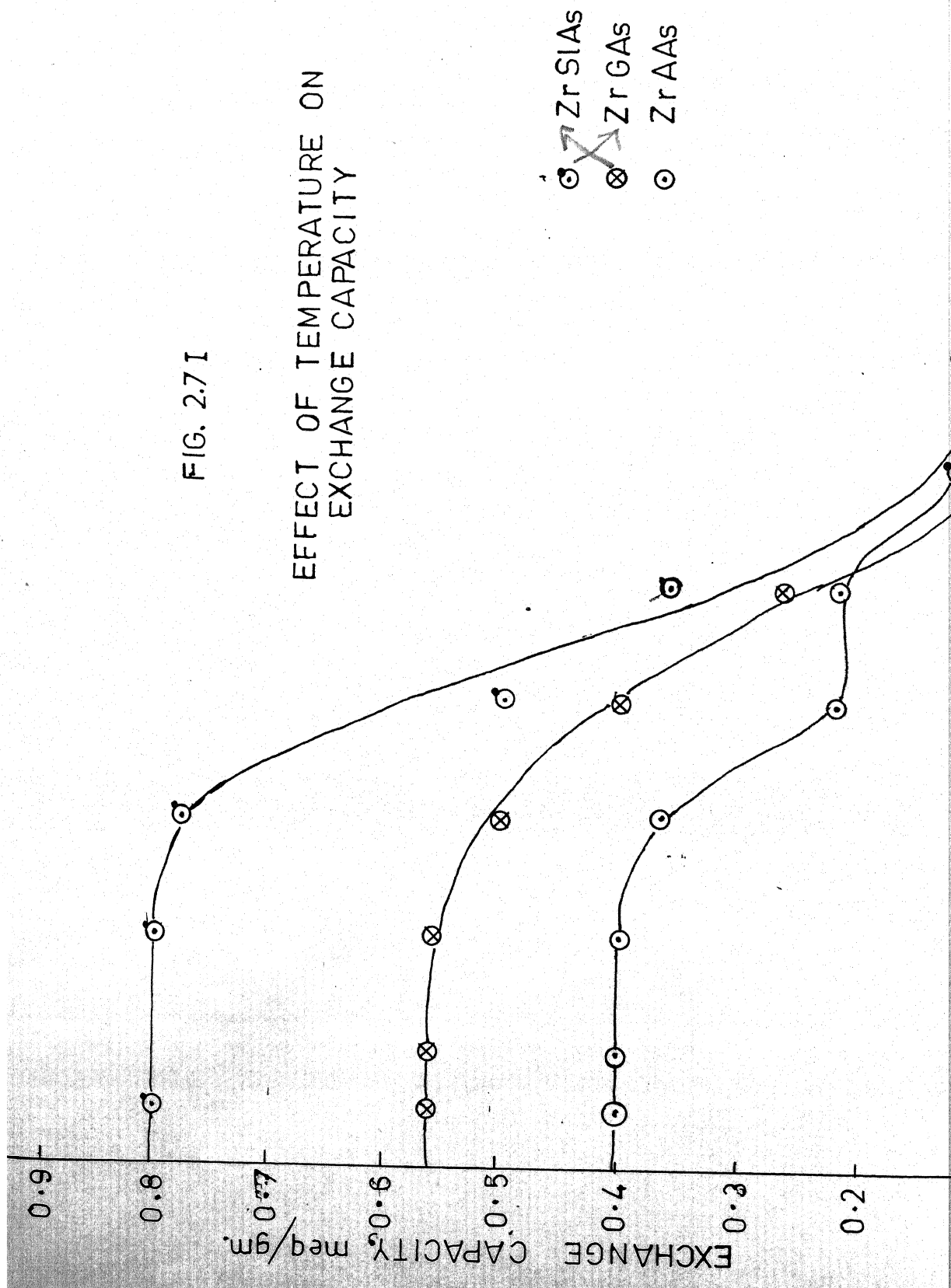


Table 2.7.1

Effect of heating on the limiting exchange capacities of the synthetic exchangers

Temperatures °C	ZrGAs	ZrSlAs	ZrAAs
25°	0.82	0.54	0.40
50°	0.82	0.50	0.40
100°	0.78	0.56	0.40
150°	0.78	0.36	0.36
200°	0.50	0.20	0.22
250°	0.36	0.20	0.22
300°	0.12	0.06	0.12
350°	0.08	0.06	0.12
400°	0.08	0.06	0.06

Table 2.8.1

Effect of ratio variation of acids in synthetic exchangers on capacity

Exchanger	Ratio Zr;Acid;AsO ₄	Capacity, meq/gm
ZrGAs	1 ; 0.5 ; 1	0.34
	1 ; 1.0 ; 1	0.79
	1 ; 1.5 ; 1	0.72
	1 ; 2.0 ; 1	0.73
ZrSlAs	1 ; 0.5 ; 1	0.29
	1 ; 1.0 ; 1	0.56
	1 ; 1.5 ; 1	0.50
	1 ; 2.0 ; 1	0.49
ZrAAs	1 ; 0.5 ; 1	0.28
	1 ; 1.0 ; 1	0.40
	1 ; 1.5 ; 1	0.40
	1 ; 2.0 ; 1	0.39

Table 2.9.1

Swelling characteristics of ZrGAs in water-ethanol
media

S. No.	Solvent Composition	Resign volume Before adding the solvent ml	Resign volume before adding the solvent ml	Swelling %
1.	water 100%	0.79	0.80	+1.26
2.	water 50%- ethanol 50%	0.82	0.79	-3.65
3.	water 50%- ethanol 75%	0.81	0.78	-3.70
4.	ethanol 100%	0.84	0.81	-3.56

Table 2.9.2

Swelling characteristics of ZrSlAs in water-ethanol media

S. No.	Solvent Composition	Resign volume Before adding the solvent ml	Resign volume after adding the solvent ml	Swelling %
1.	water 100%	0.75	0.77	+2.66
2.	water 50%- ethanol 50%	0.80	0.78	-2.50
3.	water 25%- ethanol 75%	0.82	0.80	-2.43
4.	ethanol 100%	0.80	0.77	-3.75

Table 2.9.3
Swelling characteristics of ZrAAs in water-ethanol
media

S. No.	Solvent Composition	Resign volume Before adding the solvent ml	Resign volume after adding the solvent ml	Swelling %
1.	water 100%	0.84	0.85	+1.19
2.	water 50%- ethanol 50%	0.83	0.81	-2.40
3.	water 25%- ethanol 75%	0.85	0.83	-2.35
4.	ethanol 100%	0.82	0.80	-2.44

Table 2.9.4

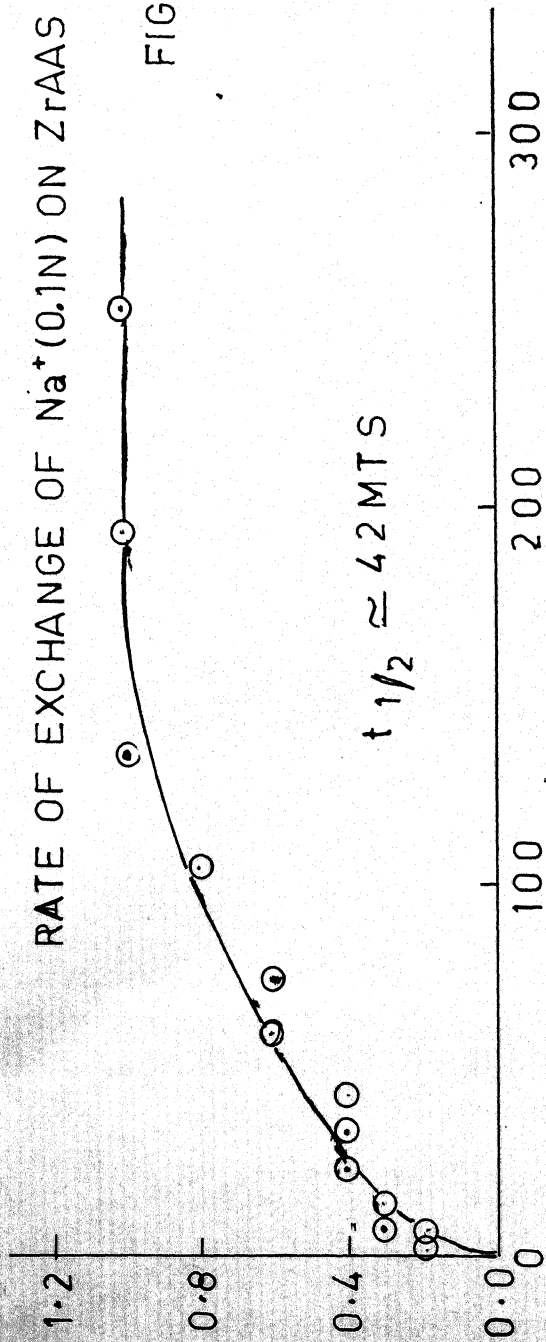
Comparative swelling characteristics of new ion exchangers

Exchanger	water 100%	water-ethanol 50% - 50%	water-ethanol 25% - 75%	ethanol 100%
ZrGAs	+1.26	-3.65	-3.70	-3.56
ZrSlAs	+2.66	-2.50	-2.43	-3.75
ZrAAs	+1.19	-2.40	-2.35	-2.44

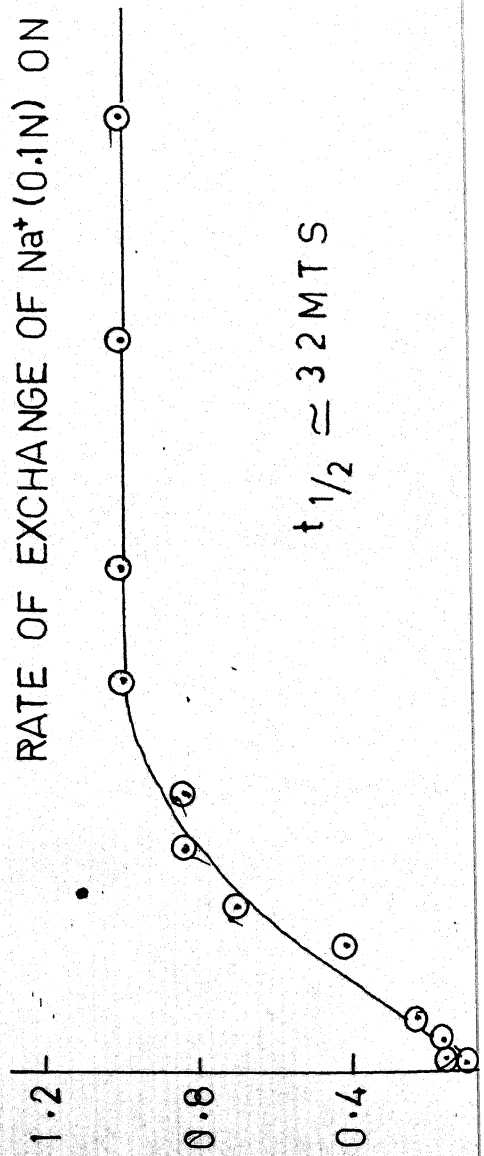
Note + swelling represents actual swelling while
- swelling shows contraction of the exchanger

RATE OF EXCHANGE OF $\text{Na}^+(0.1\text{N})$ ON ZrAAS

FIG. 2.10 II



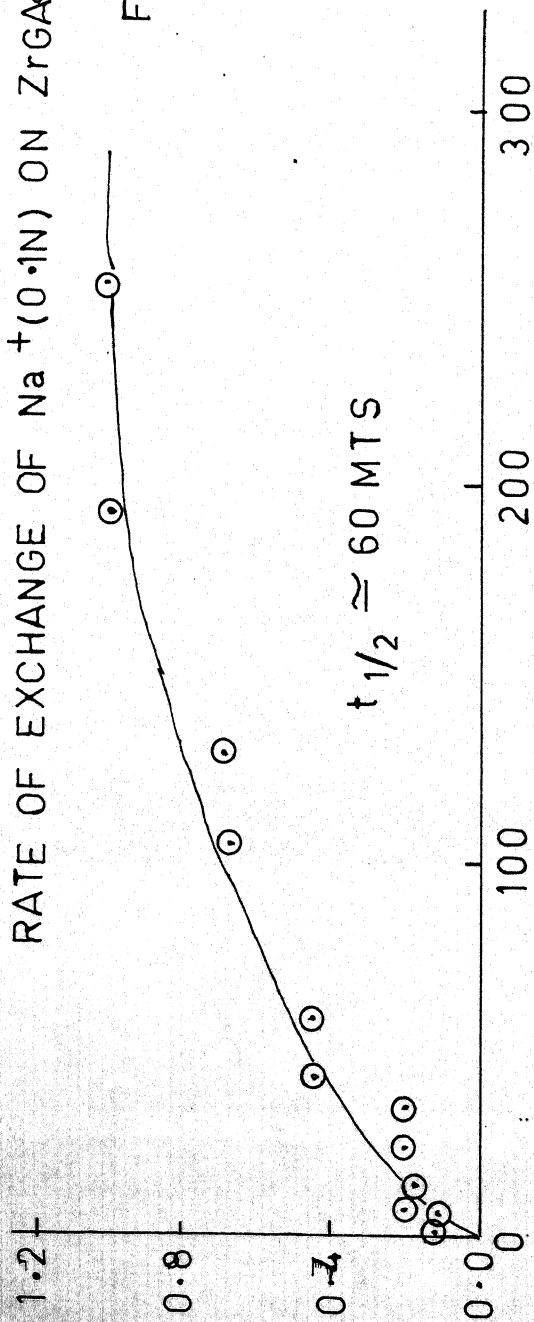
RATE OF EXCHANGE OF $\text{Na}^+(0.1\text{N})$ ON ZrAAS



RATE OF EXCHANGE OF $\text{Na}^+(0.1\text{N})$ ON ZrGAs

FIG. 2.10 I

$t_{1/2} \approx 60 \text{ MTS}$



RATE OF EXCHANGE OF $\text{Na}^+(0.1\text{N})$ ON ZrSIAs

$t_{1/2} \approx 4 \text{ MTS}$

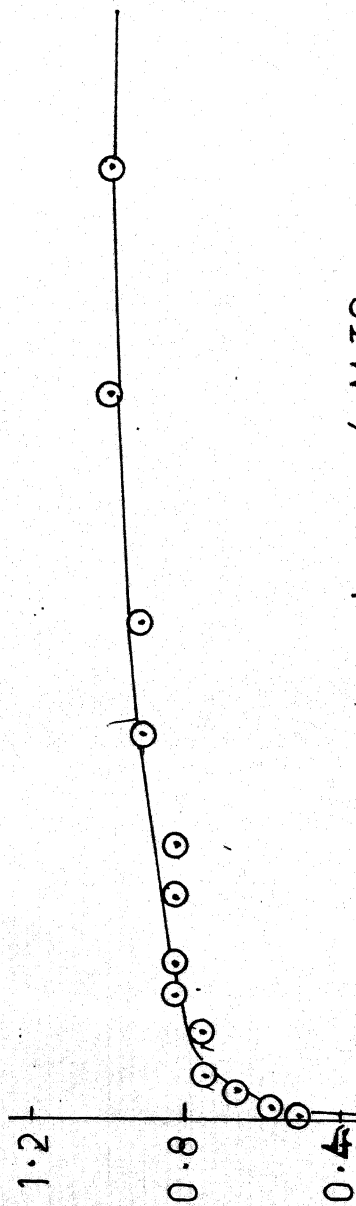


Table - 2.10.1

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Determination of rate of exchange of synthetic exchangers by using electrolyte NaCl (0.1N)

Time in mts	ZrGAs		ZrSlAs		ZrAAs	
	Meq/g exchanger	Q_t/Q_x	Meq/g exchanger	Q_t/Q_x	Meq/g exchanger	Q_t/Q_x
2	0.3	0.5	.015	.072	.05	.2
4	0.32	0.60	.05	.14	.05	.2
10	0.42	0.65	.05	.14	.075	.3
15	0.45	0.75	.075	.22	.075	.3
26	0.45	0.75	.075	.22	.10	.4
37	0.4	0.84	.15	.42	.10	.4
44	0.55	0.83	.25	.72	.10	.4
58	0.55	0.83	.30	.85	.15	.6
76	0.55	0.83	.30	.85	.15	.6
100	0.6	1.00	.35	1.00	.25	1.0
135	0.6	1.00	.35	1.00	.25	1.0
255	0.6	1.00	.35	1.00	.25	1.0
over night	0.6	1.00	.35	1.00	.25	1.0

t_{1/2} ≈ 4 MTS

Table 2.10.2

Time for attaining equilibrium and that for half reaction ($t_{1/2}$)

Equilibrium time in mts (Graphical)	ZrGAs	ZrSlAs	ZrAAs
	220	130	194
$t_{1/2}$ mts (Graphical)	48	32	42

CHAPTER - T H R E E

- 3.1 General Introduction
- 3.2 Affinity sequences in Inorganic exchangers
- 3.3 The present studies
- 3.4 Experimental
- 3.5 Results
- 3.6 Discussion
- 3.7 References.

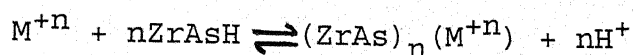
3.1 General Introduction

According to the general definition of ion exchange, the process is a reversible interchange of ions taking place between an ion in solution and another in the exchanger which is insoluble in the medium. Hence the process can be represented by the general equation given below:



where R^- represents the polymer network of the exchanger which bears an exchangeable ion A^+ , while B^+ is an ion in solution.

The same can be modified and can be written again as follows of an inorganic exchanger like zirconium arsenate or any zirconium based exchanger.



Here M^+ is the metal ion under exchange and $ZrAsH$ represents the zirconium arsenate exchanger with replaceable H^+ . The above reaction can be treated for the evaluation of its equilibrium constant; applying law of mass action to give

$$K = \frac{[\bar{M}^{+n}] [H^+]^n}{[M^{+n}] [\bar{H}^+]^n} = \frac{[\tau M^{+n}] [\tau H^+]^n}{[\tau M^{+n}] [\tau H^+]^n}$$

In this equation all barred terms indicate the resin phase values, while the others as solution phase values. The square brackets denote the concentrations, while the τ terms give the activity coefficients. It has been pointed out that for exchanges involving trace amounts, the exchange is reversible for most of the metal ions (1,2,3) under these conditions the concentration of the metal ion M^+ is very small as compared to H^+ in the ex-

changer and therefore extent of exchange is sufficiently small. The variations in the H^+ concentration can be ignored under these conditions and pH variations are thus negligible. Moreover in such dilute solutions the activity coefficient terms can also be assumed to be constant.

Thus for trace amount exchanges $K = \frac{[\bar{M}^{+n}]}{[M^{+n}]}$ which is nothing but distribution coefficient (K_D).

By using this value for K_D , the distribution coefficient, the above general equation for equilibrium constant, can be put as

$$\log \frac{[\bar{M}^{+n}]}{[M^{+n}]} = npH + \log K + n \log C$$

where $C = [H^+]$ and activity coefficient have been ignored because of low concentrations and reversibility of the reaction. Thus a plot of $\log K_D$ against pH will yield a straight line of slope -n.

Many exchange reactions such as those between Br^-/NO_3^- on hydrous zirconium oxide and Ba^{2+}/NH_4^+ on zirconium tungstate(4) show the applicability of this relationship. But when exchanges involving Cs^+ , UO_2^{2+} and Ce^{3+} ion are studied, deviations have been found out. In such cases the distribution coefficient increases with decreasing exchanger loading at constant pH. These ions have high affinity for certain other functional groups in the exchanger, which are present in small amounts (~ 0.003 meq/gm).

The above considerations show that the two typical quantities represent the extent of exchange are (1) the equilibrium constant and (2) the distribution coefficient. The equilibrium constant truly defines the exchange for perfectly

reversible reactions; but since the activity coefficients for most ions in solution phase and for cases in exchanger phase are still a difficulty with experimental, the simpler term, selectivity coefficient (K_a) has been used to show the extent of exchange in practically all cases. Thus the selectivity coefficient K_a for the two ions A and B can be written as

$$K_a = \frac{[\bar{B}^+][A^+]}{[B^+][\bar{A}^+]}$$

where again the barred quantities are the concentrations of the two ions in the exchanger phase, while the other terms are for the solution phase.

The distribution coefficient K_D is related to K_a as below

$$K_D \approx K_a \frac{q_0}{C_0}$$

where q_0 is the capacity of the exchanger in meq/gm and C_0 is the initial concentrations of the solution in meq/ml in which the exchanger is immersed. Naturally the metal ion distribution on the exchanger is inversely proportional to the solution concentration.

3.2 Affinity Sequences in Inorganic Exchangers

Now it is clear that the extent of exchange can be represented by K_a and this can be taken as a measure of affinities of the exchanging ions of an exchanger under particular fixed conditions of experiment (i.e. exchanger quantity, solution concentration, solvent type etc.)

In organic exchangers of the synthetic type, namely the

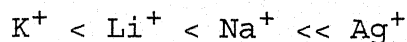
zeolite and zirconium phosphate type exchangers. The affinity of an ion for the exchanger is a function of the exchanger type (i.e. dependent on the structure, crystalline and amorphous form, its sieve action etc.)

Thus for zeolites the affinity varies rather unpredictably and is strongly dependent on the cationic composition of the exchanger. At equivalent loading's of both the counter ions the sequence of affinity in chabazite is as follows



The affinity of potassium is always very great as compared to Na at all compositions ie $\text{K}^+ \gg \text{Na}^+$ (for chabazite)

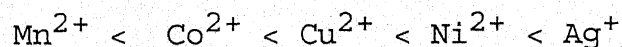
In sodalite (basic) the increasing affinity sequence is



Though no reasoning can be provided for such a random selectivity patterns in zeolites, yet their use in analysis and trace recovery has been made. Thus basic sodalite can be used for quantitative of Ag^+ .

Synthetic ultramarine has been used to separate francium (223) from its actinium parent(5), on account of higher affinity of highly charged Ac-237, Th-237, Po-215 and Pb-211, while Fr-223, Tl-207 and Ra-223 show lesser affinities and pass out the exchanger column.

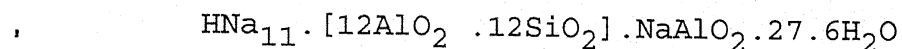
The exchange affinity of mono and divalent ions for sodium ultramarine (b) varies as below:



Here if Ag^+ is not considered, then the sequence to the increasing affinities is corresponding to the decreasing ionic radii of the concerned ions.

The mineral clinoptilolite has a higher affinity for Cs^+ when exchanged against Na^+ as compared to its affinity for montmorillonite.

A material called Luide sieve 4A(7) has been used to study the mechanism of exchange for the set of alkali metal ions. This material has a small amount of hydrogen ion even in its sodium form and can be represented as



The relative affinity series for alkali metals for this exchanger is $\text{Cs}^+ < \text{Li}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+$. This shows that the affinity here increases with decreasing crystal radius (except for Li^+). The exchanger can be converted to its K^+ or Li^+ forms completely but Rb^+ and Cs^+ forms are obtained only as partially converted forms probably due to steric reasons.

The different forms can be represented as below

Lithium form : $\text{HLi}_{11} \text{ X} \cdot \text{LiAlO}_2 \cdot 26 \cdot 3\text{H}_2\text{O}$

Potassium form: $\text{HK}_{11} \text{ X} \cdot \text{KAlO}_2 \cdot 24 \cdot 7\text{H}_2\text{O}$

Rubidium form: $\text{HRb}_{8.4} \text{ Na}_{2.6} \text{ X} \cdot \text{NaAlO}_2 \cdot 23 \cdot 5\text{H}_2\text{O}$

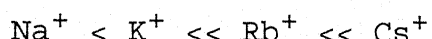
Ceasium form : $\text{HCs}_{5.4} \text{ Na}_{5.6} \text{ X} \cdot \text{NaAlO}_2 \cdot 21 \cdot 8\text{H}_2\text{O}$

Thus it is clear that the affinities of different ions for zeolites are not dependent on any fixed criterion, but it appears to be influenced by the structural considerations of the material used. Outwardly the factors affecting affinity appear to be very complex.

The exchange in hetropoly acid salts, such as ammonium molybdophosphate, ammonium molybdo-arsenate, ammonium tungstophosphate etc. pointed out certain other peculiarities. For

example it has been pointed out that the replacement of NH_4^+ in the compound such as $(\text{NH}_4)_3\text{PMO}_{12}\text{O}_{40}$, by sodium is least efficient(8,9) and potassium replaces it only to an extent of about 2/3 of the total ammonium ions(10). Hence the affinity sequence for molybdophosphates for heavier alkali metal cations is given(11) as $\text{K}^+ < \text{Rb}^+ < \text{Cs}^+$

Smit(12) has given this sequence on the basis of distribution coefficient values for ammonium-molybdophosphate as below:



The values for Cs^+ are very high, say about 6000 more than Na^+ which has zero distribution coefficient on this exchanger.

Smit et al(13) have also studied such distributions several other 12-hetropoly acid salts in tracer concentrations in 0.1N NH_4NO_3 . The general observations show that the uptake of the trace ion is increased as the radius of the unhydrated ion increases. Thallous and silver(I) ions are held more strongly than alkali metal cations of similar size possibly due to some degree of covalency in the bonding. Multivalent cations showed negligible exchange in acid solutions but were strongly absorbed from neutral solutions (some as simple ions, others as complexed species)

In such exchangers the structure of the exchangers the structure of the exchangers is such that large monovalent cations(K^+ , Rb^+ , Cs^+ , Tl^+ , As^+) pack stably in to it, give insoluble crystal. But salts containing other alkali metal cations are soluble and are unsuitable for exchange purpose.

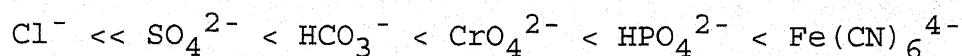
Though the distribution of alkali metal ions is inde-

pendent of pH between 1.1 to 4.5 but transition metal ions are influenced by it.

The hydrous oxides form a different series of inorganic exchangers. Freshly precipitated trivalent metal oxides (eg. hydrous ferric oxide and ferric hydroxide) readily absorb alkaline earth cations (14,15) are absorbed above pH 7.

It is said that alkali and alkaline earth metal ions are sorted on the surface, while the highly charged ions as Ce^{3+} , Ru^{4+} are sorbed in bulk(17).

The use of amphoteric oxides show that absorption depends on the pH of the solution and the effect is more of a surface phenomenon than any other thing. Al_2O_3 at proper pH is good for separating metal ions existing as anions(eg. Mo-99, Te-99, Te-132). The affinity series for anions is as below for magnetite(18).

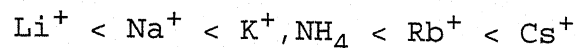


Alkali metal cation exchange studies (19) with hydrous $\text{Mn}(\text{OH})_2$ have given the following affinity series $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{NH}_4^+ < \text{Cs}^+$

The quadrivalent oxides such as SnO_2 , ThO_2 , TiO_2 and ZrO_2 act both as cation and anion exchangers depending upon the pH of the solution. In acidic solutions ThO_2 and ZrO_2 act as anion exchangers but they can also absorb UO_2^{2+} , Fe^{3+} and Cr^{3+} and to a lesser extent Ni^{2+} and Cu^{2+} ions between pH values 2-5 (20,21) hydrous silica oxide behaves only as cation exchanger. Ions of charges up to +3 (Na^+ , Ca^{2+} , UO_2^{2+} , Gd^{3+}) are exchanged rapidly by this type of exchanger. But more highly charged ions

as Zr^{4+} , U^{4+} , Pu^{4+} , are absorbed slowly.

Let us now talk about the zirconium phosphate, the very well studied compound prepared in variety of forms to get an inorganic exchanger. The selectivity for univalent cations is given as below (1,2,4)

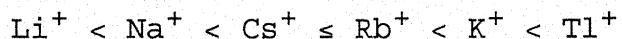


which is similar in pattern to that given by sulphonic acid type organic resins.

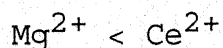
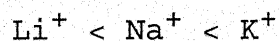
The same is true for alkaline earth metal ions. The sequence of affinity is $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$ which is given from the distribution data on an acid form of the zirconium phosphate at $\sim 0.014\text{N}$ concentration (1,4).

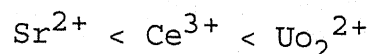
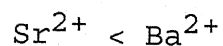
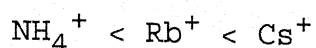
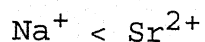
In zirconium vanadate the rare earths show absorption to varying extents (22). Zirconium antimonate (23) shows the reversal in selectivity for sodium and potassium ions. The selectivity order is $\text{Li}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{Na}^+$.

The selectivity increases for several ions when the zirconium phosphate samples heated at different temperatures are used. Distribution coefficients for a number of cations increases to different extent as a result of heating. The magnitude of increase in distribution values varies in the following order



Baetsle (24) has shown from exchange studies on amorphous zirconium phosphate that the affinities are as per the sequence of hydrated ionic sizes. The following sequences have been given for the gels from trace studies for several ions (3,24,25,26)





Macro level studies were carried out by Baetsle and Huys(2) for Na^+ , K^+ , Ca^{2+} , and Sr^{2+} with hydrogen on a zirconium phosphate exchanger. Results agreed well with those obtained at trace level.

Lassen and Vissers(25) have shown for exchanges of Li^+/H^+ , Na^+/H^+ and K^+/H^+ system at $\text{pH} = 1$ using a capacity measured at $\text{pH} = 5$, that in none of the systems, the fraction of the metal ion on exchanger exceeded 35% of the capacity.

3.3 The Present Studies

This part of the work deals with ionic exchange affinity studies for some unipositive ions on the newly prepared exchangers. It has been shown in the earlier section that different types of inorganic exchangers show different affinity behavior for various ions. In simple zirconium based exchangers, the affinity of univalent ions changes its sequence under different conditions or when sample heated at different temperatures are used. Hence it is essential that the newly prepared samples of inorganic exchangers should be studied from the point of view of their selectivity for the ions of different types. Here the univalent ions from four alkali metals, thallous and silver have investigated for their affinities towards three exchangers, namely ZrGAs, ZrSlAs and ZrAAs..ls1

Experiments have been carried out with electrolyte solutions of different ionic concentrations to get the selectivity coefficient data for these ions. Thus metal ion solutions of ionic concentrations between 0.005N to 0.1N have been used in these studies to provide different ionic loadings.

The ions that have been investigated include Li^+ , Na^+ , K^+ , Cs^+ , Tl^+ and Ag^+ . The method of investigation is the batch technique or the static equilibrium exchange procedure with fixed quantity of the exchanger and total electrolyte solution volume.

3.4 Experimental

Metal ion solutions were prepared from their Analar nitrates so as to give their stock solutions of 0.1N strength. These were suitably diluted to prepare 0.07, 0.05, 0.03, 0.01 and 0.005N solutions for equilibrium studies.

Always 0.25 gm of the exchanger was taken in an Erlenmeyer flask of 150 ml capacity. Exactly 50 ml electrolyte solution of proper ionic concentration was added to it and the flask was stoppered properly. Different batches were prepared in the same way to equilibrated different exchanger samples with different metal ion solutions of varied strengths. These flasks, suitably numbered for identification were kept for ~24 hours with intermittent shaking to keep the solid and solution phases well in contact.

After equilibration aliquots (5ml) from the supernatant liquids in each flask were with drawn and estimated suitably for the exchanged ion. Thus in cases of exchangers involving alkali

metals and thallous ion, the released hydrogen ion was estimated titrimetrically, while in the case of silver ion, the ion itself was estimated by using ammonium thiocyanate as the titre with ferric ion as indicator. Thus the extent of exchange in each case was evaluated for all ions studied. Knowing this and the exchange capacities of the exchangers used apparent equilibrium constants were calculated as shown below.

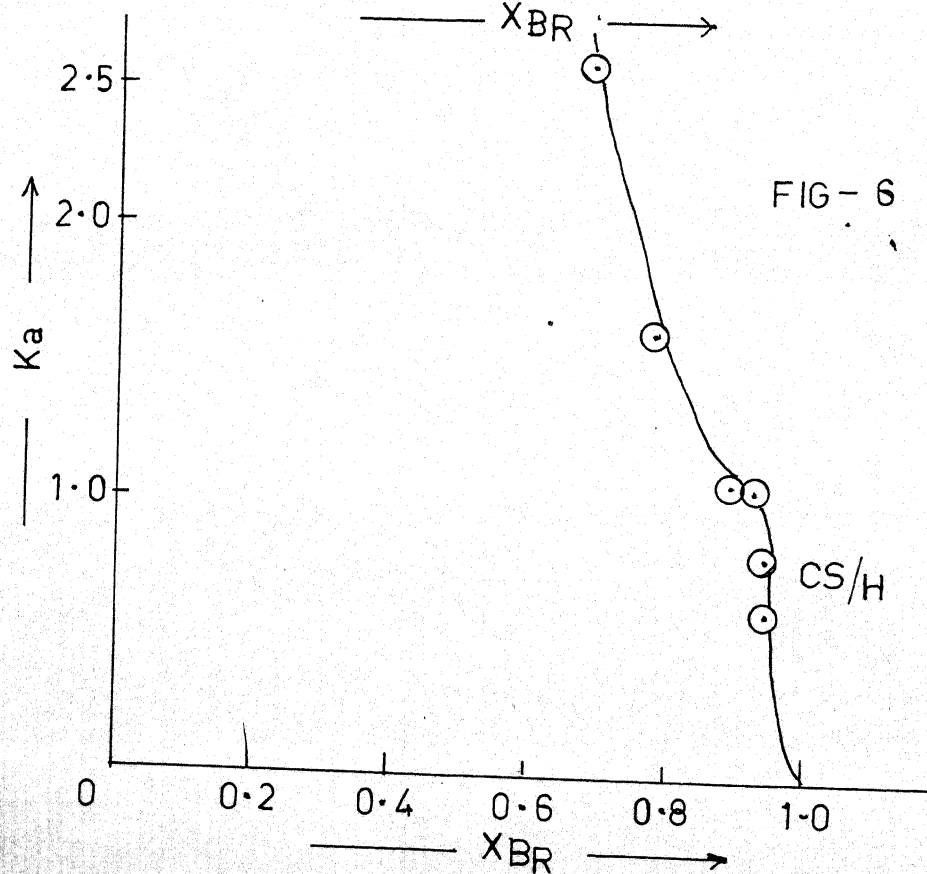
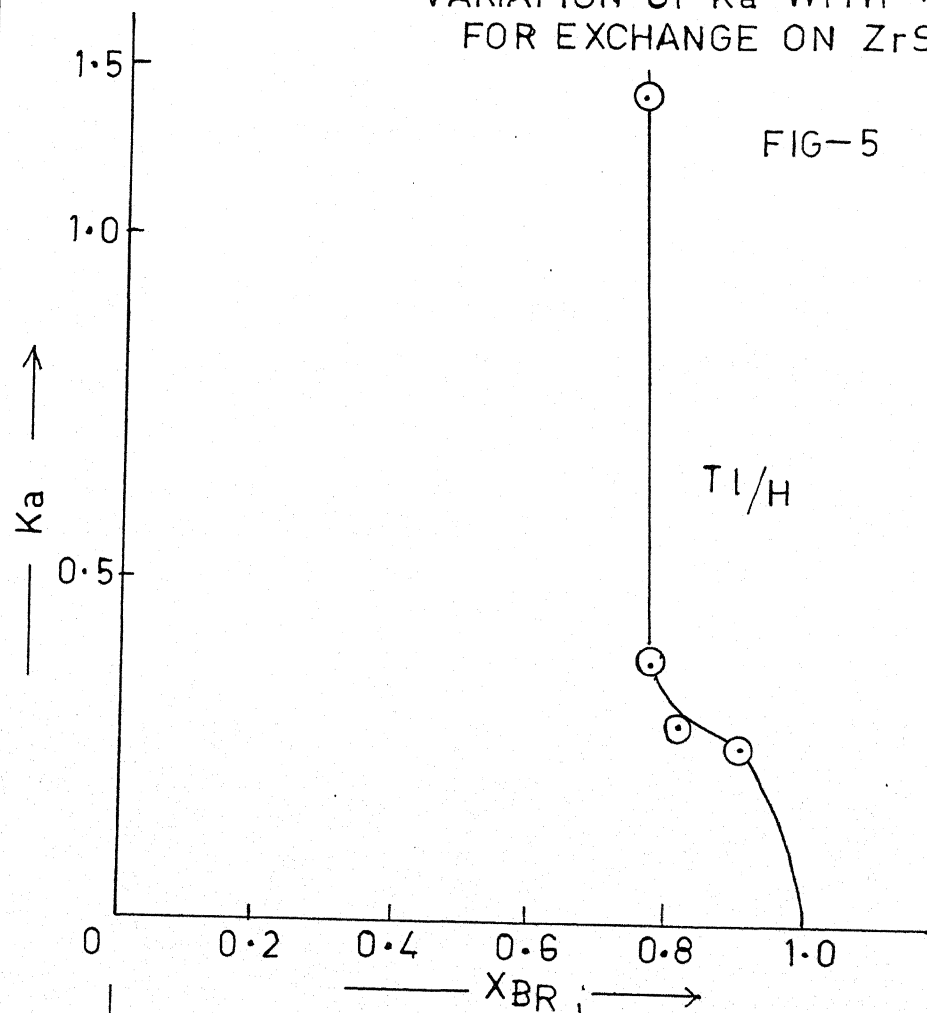
In an inorganic exchanger, the use of law of mass action can be made as usual to evaluate the values of K_a , the apparent equilibrium constant or the selectivity coefficient as

$$K_a = \frac{X_{BR}}{X_{AR}} \cdot \frac{C_{AW}}{C_{BW}}$$

where X_{BR} and X_{AR} terms represent the equivalent fractions of exchanged ion and hydrogen ion in the exchanger at equilibrium, while C_{AW} and C_{BW} are the concentrations terms for hydrogen and the exchanging counter ion in the solution phase. The relationship has been used by Kressman and Kitchener(27) for evaluating selectivity coefficients in case of organic ion exchangers.

The results at different ionic loadings have been tabulated in tables 3.5.1 to 3.5.18 for all the ions for the newly prepared exchangers.

VARIATION OF K_a WITH X_{BR}
FOR EXCHANGE ON ZrSLAs



VARIATION OF K_a WITH X_{BR}
FOR EXCHANGE ON ZrSIA's

FIG-3

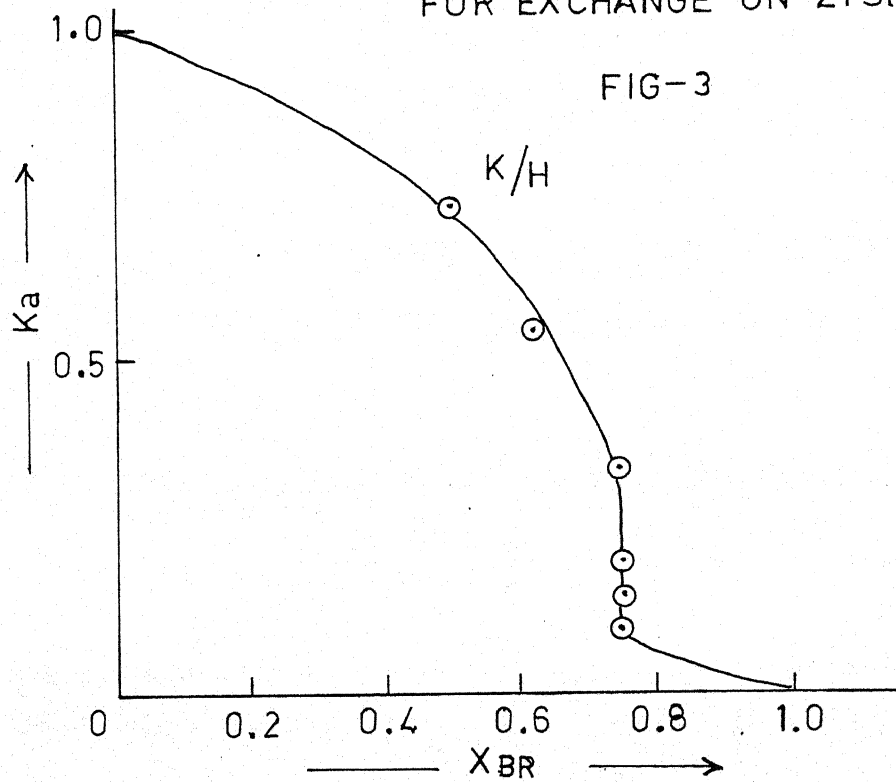
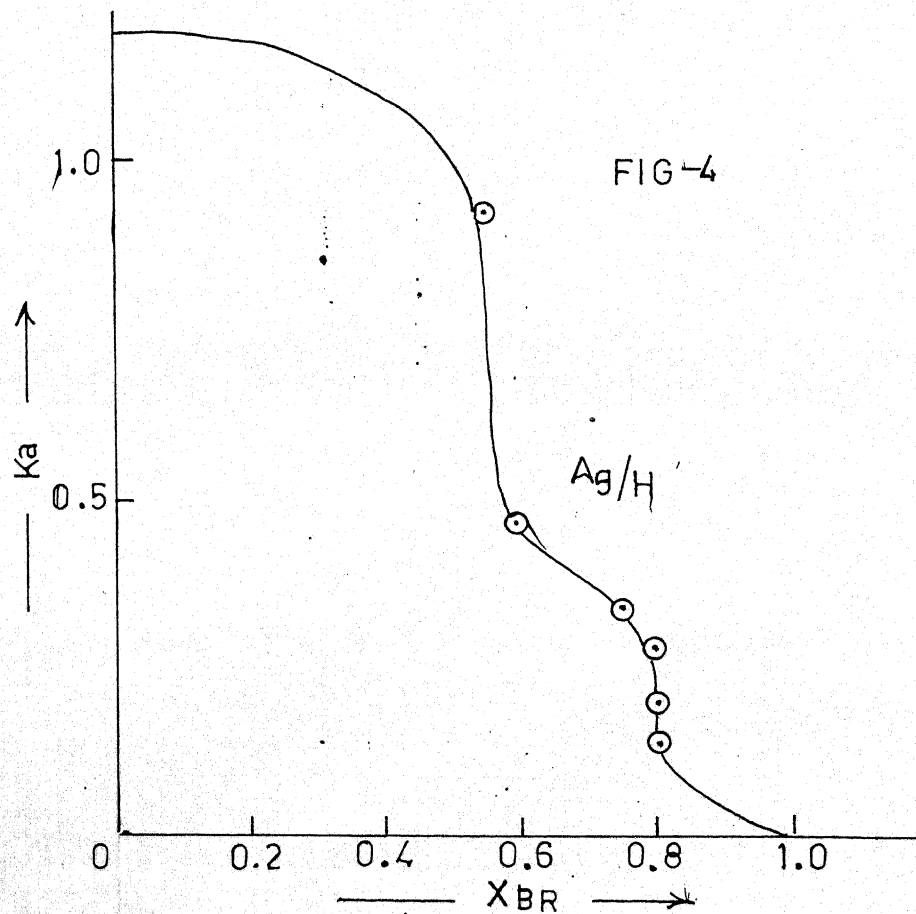


FIG-4



VARIATION OF K_a WITH X_{BR}
FOR EXCHANGE ON Zr SIAS

FIG - 1

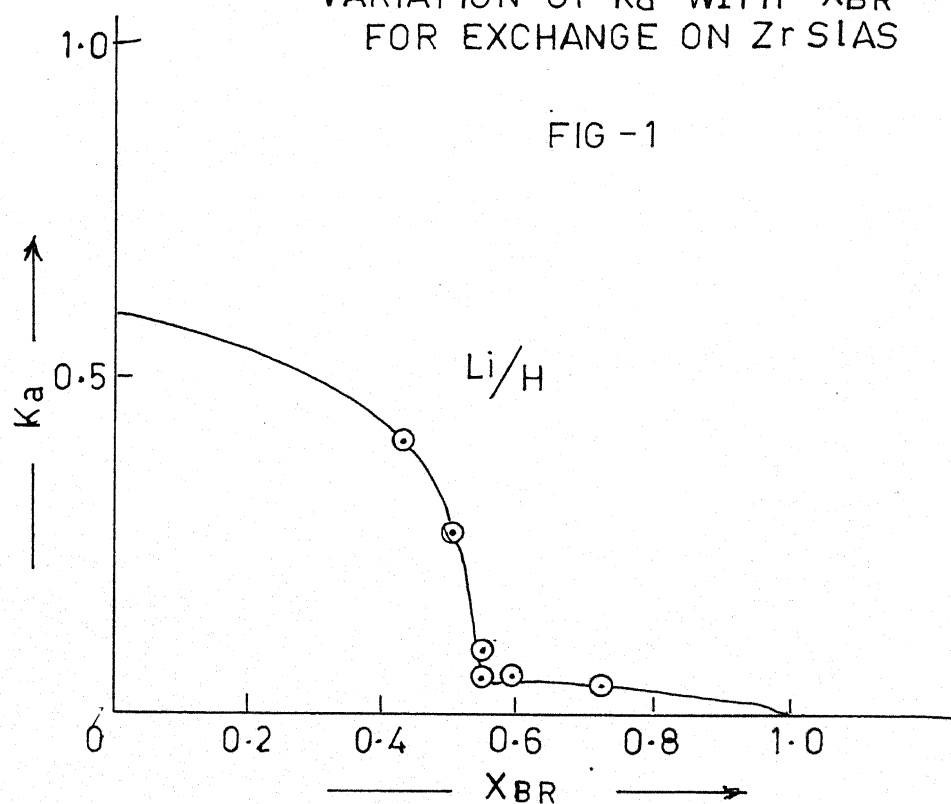


FIG - 2

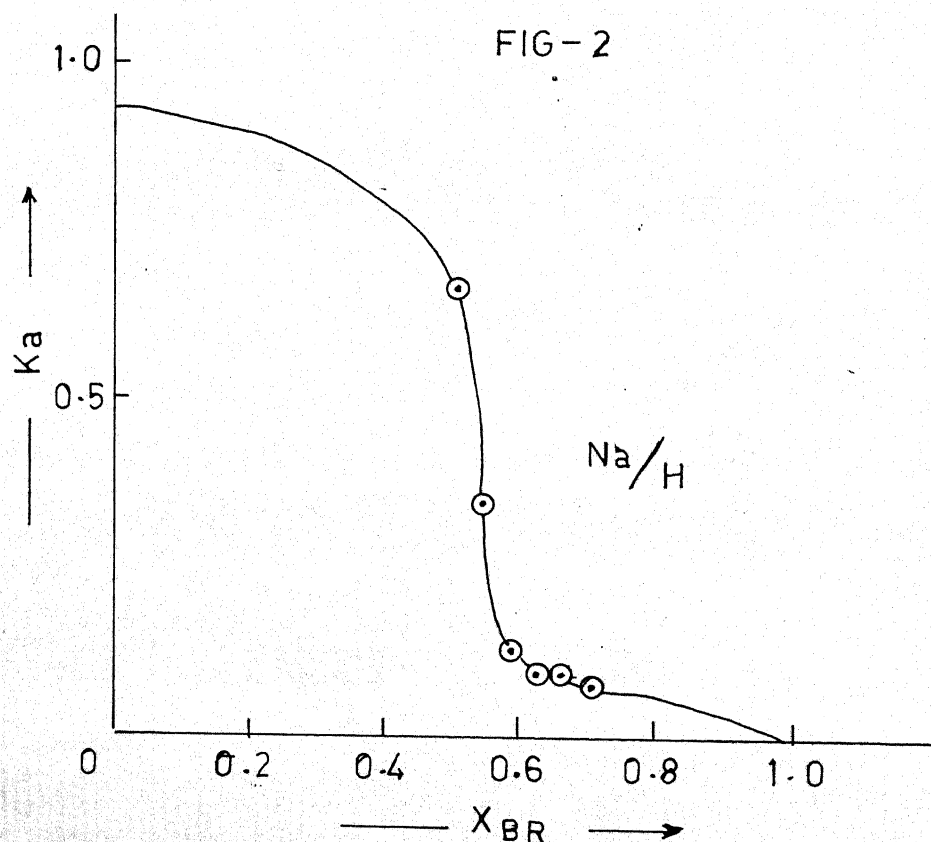


Table 3.5.1

Exchange of Li^+ ion against H^+ ion in ZrGAs exchanger

meq added	X_{BR}	Ka
0.25	0.46	0.30
0.5	0.58	0.20
1.5	0.64	0.18
2.5	0.70	0.10
3.5	0.70	0.072
5.0	0.70	0.050

Table 3.5.2

Exchange of Na^+ ion against H^+ ion in ZrGAs exchanger

meq added	x_{BR}	Ka
0.25	0.50	0.38
0.5	0.57	0.23
1.5	0.71	0.17
2.5	0.78	0.18
3.5	0.78	0.10
5.0	0.78	0.080

Table 3.5.3

Exchange of K^+ ion against H^+ ion in ZrGAs exchanger

meq added	X_{BR}	K_a
0.25	0.58	0.50
0.5	0.64	0.36
1.5	0.71	0.32
2.5	0.80	0.19
3.5	0.80	0.13
5.0	0.80	0.09

Table 3.5.4

Exchange of Ag^+ ion against H^+ ion in ZrGAs exchanger

meq added	x_{BR}	K_a
0.25	0.57	0.62
0.5	0.71	0.61
1.5	0.78	0.28
2.5	0.78	0.28
3.5	0.85	0.20
5.0	0.85	0.139

Table 3.5.5

Exchange of Tl^+ ion against H^+ ion in ZrGAs exchanger

meq added	X_{BR}	Ka
0.25	0.69	1.42
0.5	0.76	0.86
1.5	0.80	0.32
2.5	-	-
3.5	-	-
5.0	0.80	0.2

Table 3.5.6

Exchange of Cs^+ ion against H^+ ion in ZrGAs exchanger

meq added	x_{BR}	Ka
0.25	0.80	2.80
0.5	0.84	1.6
1.5	0.94	1.5
2.5	-	-
3.5	-	-
5.0	0.98	1.2

Table 3.5.7

Exchange of Li^+ ion against H^+ ion in ZrSlAs exchanger

meq added	X_{BR}	K_a
0.25	0.30	0.090
0.50	0.30	0.0409
1.5	0.40	0.0229
2.5	0.44	0.01767
3.5	0.48	0.0161
5.0	0.52	0.0144

Table 3.5.8

Exchange of Na^+ ion against H^+ ion in ZrSlAs exchanger

meq added	x_{BR}	Ka
0.25	0.50	0.295
0.50	0.48	0.120
1.5	0.52	0.049
2.5	0.56	0.036
3.5	0.60	0.032
5.0	0.60	0.022

Table 3.5.9

Exchange of K^+ ion against H^+ ion in ZrSlAs exchanger

meq added	x_{BR}	Ka
0.25	0.56	0.490
0.5	0.56	0.207
1.5	0.60	0.0789
2.5	0.64	0.058
3.5	0.64	0.0415
5.0	0.64	0.028

Table 3.5.10

Exchange of Ag^+ ion against H^+ ion in ZrSlAs exchanger

meq added	X_{BR}	Ka
0.25	0.64	0.72
0.50	0.72	0.56
1.5	0.72	0.16
2.5	0.80	0.16
3.5	0.80	0.11
5.0	0.80	0.08

Table 3.5.11

Exchange of Tl^+ ion against H^+ ion in ZrSlAs exchanger

meq added	X_{BR}	K_a
0.25	0.68	1.09
0.5	0.80	1.00
1.5	0.88	0.58
2.5	0.88	0.33
3.5	0.88	0.23
5.0	0.88	0.16

Table 3.5.12

Exchange of Cs^+ ion against H^+ ion in ZrSlAs exchanger

meq added	X_{BR}	Ka
0.25	0.80	3.00
0.5	0.88	1.88
1.5	0.95	1.64
2.5	0.96	1.20
3.5	0.96	0.85
5.0	0.96	0.59

Table 3.5.13

Exchange of Li^+ ion against H^+ ion in ZrAAs exchanger

meq added	x_{BR}	K_a
0.25	0.42	0.128
0.50	0.45	0.080
1.5	0.50	0.034
2.5	0.55	0.027
3.5	0.55	0.019
5.0	0.55	0.012

Table 3.5.14

Exchange of Na^+ ion against H^+ ion in ZrAAs exchanger

meq added	X_{BR}	K_a
0.25	0.50	0.25
0.50	0.50	0.11
1.5	0.60	0.062
2.5	0.60	0.036
3.5	0.65	0.035
5.0	0.65	0.024

Table 3.5.15

Exchange of K^+ ion against H^+ ion in ZrAAs exchanger

meq added	X_{BR}	K_a
0.25	0.625	0.555
0.50	0.625	0.238
1.50	0.750	0.157
2.50	0.750	0.092
3.50	0.750	0.065
5.00	0.750	0.040

Table 3.5.16

Exchange of Ag^+ ion against H^+ ion in ZrAAs exchanger

meq added	X_{BR}	K_a
0.25	0.75	0.95
0.50	0.75	0.37
1.5	0.80	0.22
2.5	0.80	0.13
3.5	0.80	0.093
5.0	0.80	0.065

Table 3.5.17

Exchange of Tl^+ ion against H^+ ion in ZrAAs exchanger

meq added	X_{BR}	Ka
0.25	0.72	1.04
0.50	0.78	0.652
1.50	0.82	0.260
2.50	0.86	0.218
3.50	0.89	0.208
5.00	0.89	0.140

Table 3.5.18

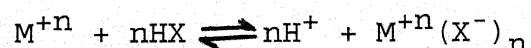
Exchange of Cs^+ ion against H^+ ion in ZrAAs exchanger

meq added	X_{BR}	Ka
0.25	0.78	1.66
0.50	0.87	1.43
1.50	0.91	0.65
2.50	0.93	0.50
3.50	0.93	0.35
5.00	0.93	0.24

3.6 Discussion

An ion exchanger shows preference for certain ions as compared some others. This tendency is referred to as the selectivity of an ion exchanger. On the other hand the ions show an affinity for an exchanger and this affinity may change for different exchangers. If the type of the exchanger is fixed then different ions show an affinity for an exchanger and this affinity may change for different exchangers. If the type of the exchanger is fixed then different ions show different affinities for the exchange's matrix. This affinity is usually called as ionic-exchange affinity and is measured in terms of the equilibrium constant of the exchange reaction.

Thus if a metal ion M^{+n} is going to be exchange for a H^+ ion in the exchanger then the process of reversible exchange can be written as



Since the process is reversible and involves stoichiometric change, the law of mass action can be applied to obtain the equilibrium constant (K) for such a reaction.

$$\text{The expression } K = \frac{[M^{+n}]_R [H^+]_w^n}{[M^{+n}]_w [H^+]_R^n}$$

then gives this constant and this may be taken as a true measure of the respective affinities of different exchangeable ions. The square brackets represents the activities of the concerned ions in the two phases (exchanger = R and solution = w)

To determine K experimentally the analysis of the two phases is needed together with the activity coefficients of the ions involved in different phases. The determination of the later

terms is difficult, or rather impossible for ions in exchanger phase, hence it is customary to use only concentrations of the involved ions in this expression neglecting the activity terms. The equilibrium constant so calculated is only an apparent equilibrium constant and is generally called as selectivity coefficient. For all practical purposes, therefore, the selectivity coefficient values are used as measures of affinities of ions.

In the present studies the selectivity coefficients (K_a) have been calculated as per the expression given by Kressman and Kitchener (27) and used much in synthetic ion-exchange resin studies. The results reported for the exchange of alkali metal ions, thallous and silver ions for the four new exchangers are given in tables from 3.5.1 to 3.5.18. In each table about 5 different sets of results have been reported for exchange at different exchange at different ionic concentrations of the metal ion in solution. Keeping the exchanger quantity fixed (0.25gm) the ionic concentrations in the external solution (volume always 50 ml) was varied from 0.005 N to 0.1 N. Thus solutions were sufficiently dilute to apply the law of mass action concept for calculating equilibrium constants without the use of activity coefficients of the ions in either phases.

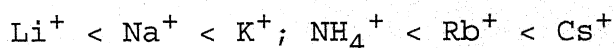
These results show very clearly that with change in ionic concentrations the equivalent fraction of the metal ion in the exchanger phase (ie X_{BR}) changed. The calculated K_a values also these different values at different ionic concentrations used for the metal ions in the external solution. This confirms for the inorganic exchangers also that K_a is not a fixed quanti-

ty. Its magnitude depends on ionic concentration or ionic loading used in exchange equilibria.

Most of the workers in this field have used K_d values by using tracer ions in presence of different macro-ion concentrations(2). When the metal ion is used at such a low concentration the values of K_d were more or less constant quantities. But at macro-level studies neither K_d is a constant valued nor K_a is a constant quantity.

The variation of K_a with X_{BR} is quite common in organic resin studies also as has been shown by several authors for different types of exchangers(28-32). The same has been proved by present studies for inorganic exchangers also. This variation of K_a with X_{BR} is quite irregular showing higher K_a values at lower concentrations and very low K_a values at 0.1M concentrations should be used for this purpose.

The following sequence of affinities on the basis of K_a values can be given for ZrGAs, ZrSlAs and ZrAAs exchangers at any of the ionic concentrations from 0.005 to 0.1N $Li^+ < Na^+ < K^+ < Ag^+ < Tl^+ < Cs^+$. For pure zirconium arsenate the general sequence given for alkali metal ion is



Although the values of distribution coefficients reported by different workers differ in detail (2,4,26); this sequence is preserved. Our results are similar. The position of Ag^+ and Tl^+ ions is also shown from our results to be after K^+ in this series Cs^+ shows quite high K_a values. Such results for Cs as well as rubidium ion have been shown by Amphlett et al (26) also.

Many attempts (33,34) have been made to explain the

differences in the ion exchange behavior of the various ions. But the most plausible explanation is based on the ionic hydration thereby. According to this theory the ions are assumed to be hydrated in aqueous solutions. The degree of hydration for cations increases with increasing charge and decreasing crystallographic radius. Since ion exchange is controlled by electrostatic forces. The adsorbability of an ion will depend on the relative charges and ionic radii of the competing ions for exchange sites in an exchanger. For ions of the same charge the relative ionic radii are the deciding factors for predicting affinity sequences.

Venny(35) tried to relate the data obtained for relative exchanges of alkali and alkaline earth ions on ion exchanging clay with the ionic radius values. An increase in relative exchange with increasing ionic radii(\AA) was shown by him. The plots were curves showing an upward trend with increasing ionic radii.

Similarly for exchange on carbonaceous zeolite Nachod and Wood(36) gave a linear relationship of equilibrium exchange with the hydrated ionic radii(\AA) for both alkali and alkaline earths the exchange increased with decreasing hydrated ionic size.

Hence, out of the two the use of hydrated ionic radii as criterion to show affinity extent is more logical. Because ions having smaller size are expected to enter the exchanger pores more easily than bigger sized ions. Li^+ ion, though smallest as unhydrated, is biggest as an hydrated ion and hence is exchanged least out of all the alkali metal ions.

We have tried to show this relationship of ionic sizes with exchange affinity measures i.e. K_a values in figures 3.6 I to IV for the 4 exchangers using K_a values from studies at 0.005N and 0.1N ionic concentrations. The trends of the curves is just similar to these obtained by Venny(35). In other words the observed exchange affinity sequence is in the increasing order of their ionic radii(naked) or decreasing order of their hydrated ionic radii. The observed sequence is thus quite logical. Therefore, it can be said that in the inorganic exchangers also the lyotropic series is obeyed when one tries to give the order of affinities for cations in dilute solutions.

While showing such relationships, it is advisable to use the time or thermodynamic equilibrium constants of individual ions as measure of their affinities for an exchanger. But when the equilibrium data is changing with ionic concentration, a method of graphical integration can be used to correct the K_a values. Such a method was suggested and used in ion exchange by Boyd et. al. (37,38).

The true equilibrium constant can be found out by the use of the following relationship.

$$\ln K = \int_{X_{BR}=0}^{X_{BR}=1} \ln K_a \cdot dX_{BR}$$

This procedure has been adopted by us also to evaluate K values for different ions. The method of graphical integration has been used for Li/H, Na/H, K/H and Ag/H exchanges using ZrSAs. The values could be evaluated here conveniently but for Cs/H or Tl/H exchanges the plots of K_a/X_{BR} were so steep that they could not

be extrapolated for values of $X_{BR} = 0$, hence the attempts failed in these cases to evaluate K .

Such values have been tabulated in the table given below (Table 3.6.1) to show the relative values of K for different ions using these values again the correct affinity sequence of these ions can be predicted and it is again the same.

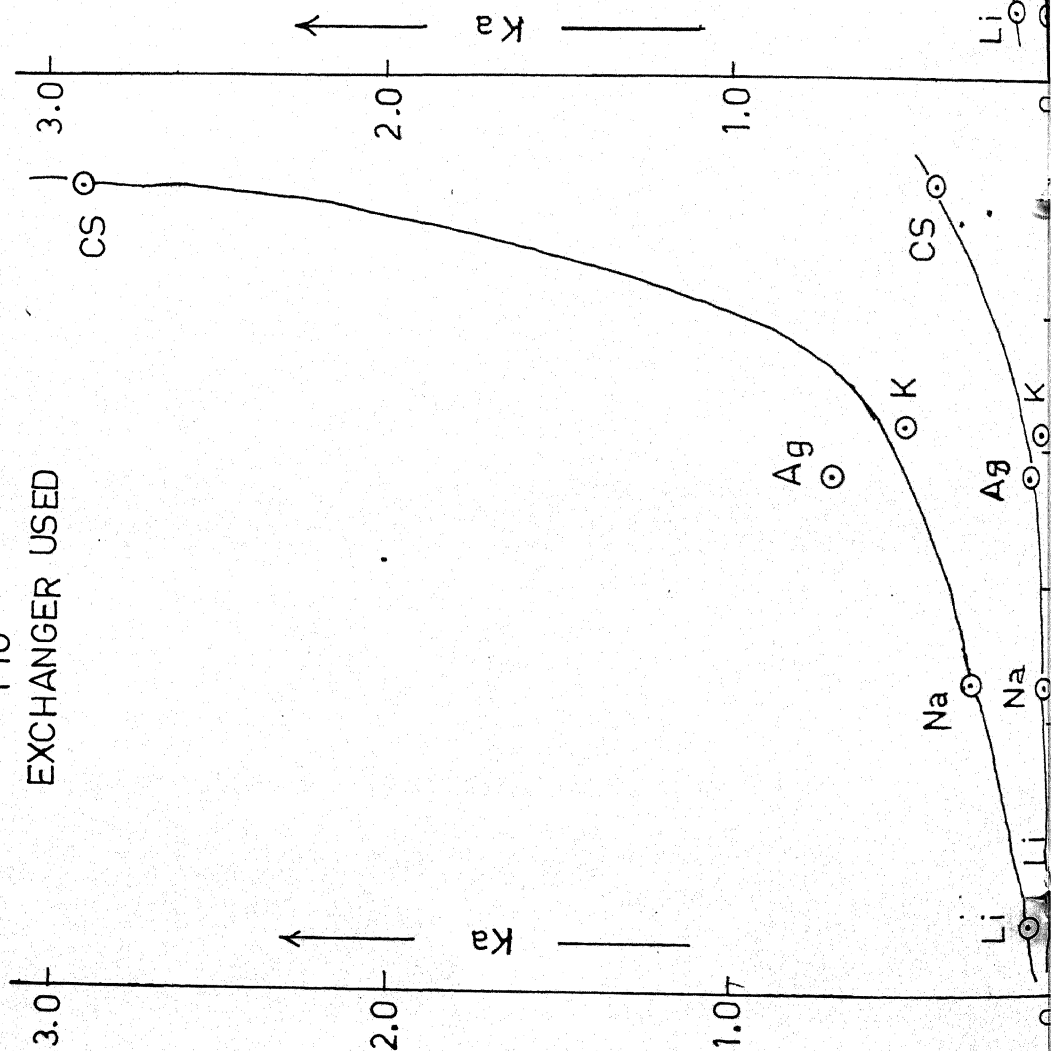
Thus the sequence of affinities for investigated univalent cations are as below for different exchangers.

1. ZrGAs $Li^+ < Na^+ < K^+ < Ag^+ \ll Tl^+$
2. ZrSlAs $Li^+ \ll Na^+ \ll K^+ < Ag^+ \ll Tl^+ \ll Cs^+$
3. ZrAAs $Li^+ < Na^+ \ll K^+ < Ag^+ < Tl^+ \ll Cs^+$

VARIATION OF K_a WITH IONIC RADIUS (\AA)

- - AT IONIC CONCENTRATION 0.005 N
- ⊗ - AT IONIC CONCENTRATION 0.1 N

FIG III
EXCHANGER USED
ZrAAs



VARIATION OF K_a WITH IONIC RADII (\AA°)

- — AT IONIC CONCENTRATION 0.005 N
- ⊗ — AT IONIC CONCENTRATION 0.1 N

FIG I
EXCHANGER USED
ZrSIAS

FIG II
EXCHANGER USED
ZrGAS

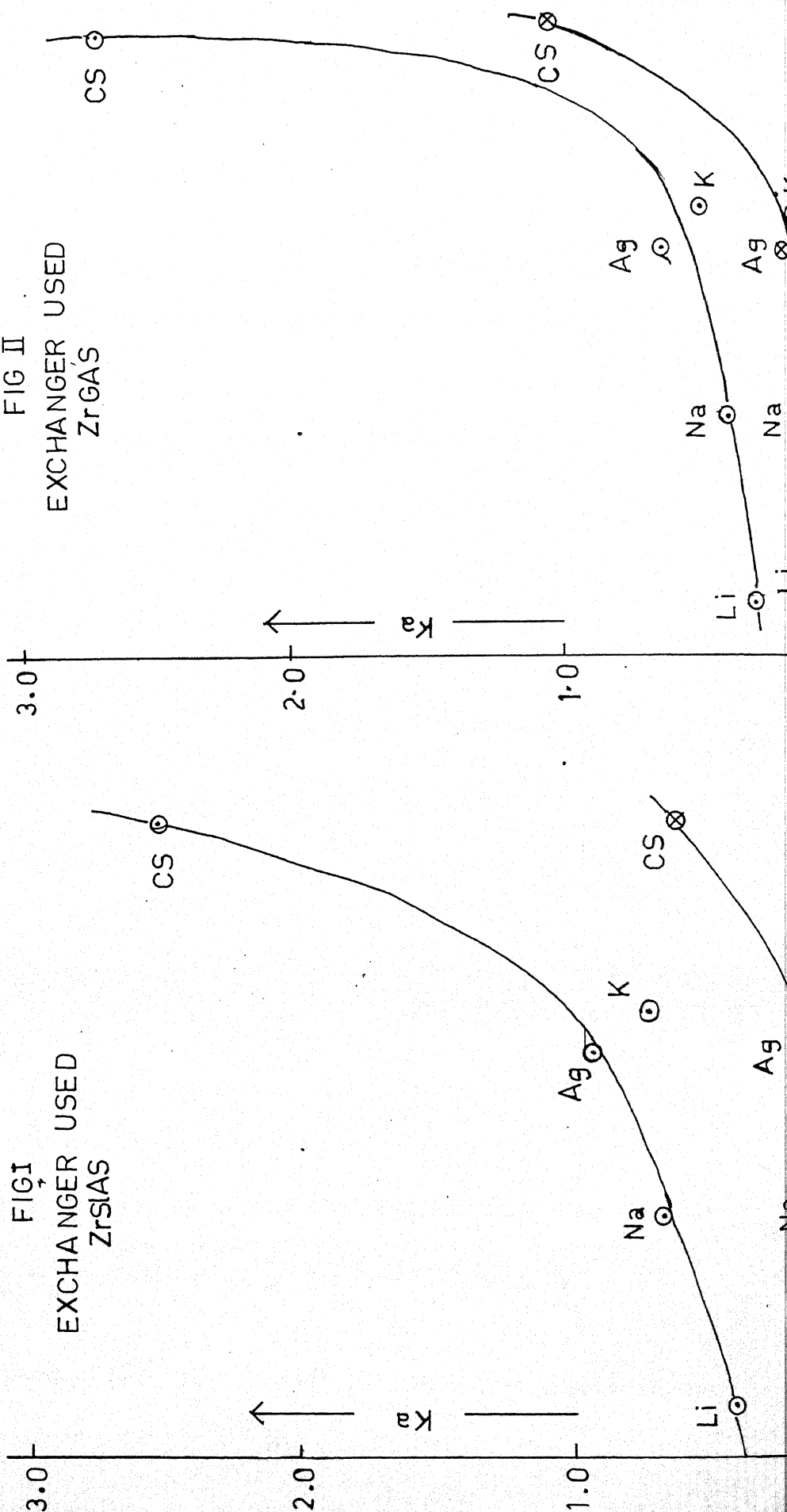


TABLE - 3.6.1

Exchanger	Ion	K
ZrGAs	Li	0.20
	Na	0.30
	K	0.48
	Ag	0.60
	Tl	1.70
	Cs	-(very high)
ZrSlAs	Li	0.04
	Na	0.30
	K	0.62
	Ag	0.78
	Tl	1.10
	Cs	4.20
ZrAAs	Li	0.08
	Na	0.18
	K	0.71
	Ag	1.20
	Tl	1.35
	Cs	1.60

In exchangers ZrGAs, and ZrSlAs Cs^+ is showing high affinity. But in ZrAAs none of these ions is showing abnormal values. Thus though the sequence of affinities is the same for this set of ions, yet their respective values (of exchange or selectivity coefficients) are different for different exchangers. The affinity for Li^+ is least in all of them and the values of K are also quite low while these for Na and K are generally in proper sequence with greater increase of Ag^+ and still greater for Tl^+ .

Exceptionally strong absorption of Cesium (and rubidium) as compared to other alkali metals has been the peculiarity of all inorganic exchangers. This has been shown by Amphlett et. al. (26) for zirconium phosphate and by Herr and Riedel (5) for zirconium phosphate, zirconium molybdate and zirconium arsenate exchangers. Even in strongly acid solutions, Cesium is very strongly absorbed by such exchangers (39). In such media it can be separated from polyvalent cations (eg. Ce^{3+} , Fe^{3+} , Pu^{4+} , UO_2^{2+} , Sr^{2+}) which show much lower absorption than cesium. Our results for Cs^+ are in accordance with these generalised conclusions about this ion.

From the present studies it can be said that in general the affinity for cations increases in the order of their decreasing hydrated-ion radius. It is so in organic ion exchange resins and also in inorganic exchangers of different types.

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CHAPTER - F O U R

4.1 Introduction

4.2 The present work

4.3 Experimental

- (A) Reagents and solutions
- (B) Titrers used
- (C) Indicators
- (D) Buffers
- (E) Exchangers
- (F) General procedure for distribution studies of metalions.

4.4 Results

4.5 Discussion and conclusions

4.6 References

Cation exchange distribution studies of some metal ions on the newly prepared inorganic exchangers (ZrSlAs, ZrGAs and ZrAAs).

4.1 Introduction

Exchanging power of a counter ion on an exchanger at equilibrium can be represented in various ways. These include (a) separation factor, (b) selectivity coefficient (c) equilibrium constant (Thermodynamic) and distribution coefficient and the thermodynamic equilibrium constant are generally used to predict the selectivity sequence of ions on the basis of equilibrium studies. But the other two namely the separation factor and the distribution coefficient are generally used in devising analytical separation procedures. The later two are easy to evaluate also as they do not involve the activities of the ions in solution and exchanger phase.

The separation factor is the quantity particularly convenient for practical applications. It is designated as α_A and defined by the expression

$$\alpha_{\frac{A}{B}} = \frac{\bar{m}_A m_B}{\bar{m}_B m_A} \text{ or } = \frac{\bar{c}_A c_B}{\bar{c}_B c_A} \text{ or } = \frac{\bar{x}_A x_B}{\bar{x}_B x_A}$$

where terms with bars are for the resin phase and the others are for the solution phase.

'm' terms, 'c' terms and 'x' terms are the ways to represent the ionic concentration. 'm' terms stand for concentrations in molarity, 'c' terms stand for concentrations in equivalents, while 'x' terms stand for concentrations as equivalent ionic fractions. This type of data are useful in calculation of column performance.

The quantity called as the distribution coefficient (K_d) is of much use in comparing the relative exchangeabilities of the counter ions. It is useful in planning separations of analytical interest. It is defined as

$$K_d = \frac{\bar{m}_i}{m_i}$$

where the distribution coefficient will be called as the molal distribution coefficient. But if the concentrations are represented as equivalents then K_d can also be written as

$$K_d = \frac{\bar{C}_i}{C_i}$$

These coefficients increase with dilution of the external solution or with decrease in 'm' and 'c' values for the ionic species 'i'.

However, for all practical purposes the distribution coefficients under given conditions can be calculated from the concentration of the counter ion in the two phases. These concentrations can be given for certain fixed weight of the resin or for a certain fixed volume of the resin. As such two types of K_d values - weight distribution coefficients and volume distribution coefficients have been reported in literature. The weight distribution coefficient is given by the relationship given below and has been used through out this work.

$$K_d = \frac{\text{meq. metal in per gm. of dry resin}}{\text{meq. metal ion per one ml. of the solution}}$$

The distribution coefficient (K_D) for a counter ion 'B' can be related to the selectivity coefficient (K_a) by the relation

$$K_D = K_a \frac{1/a [\bar{A}]^{b/a}}{[A]}$$

since

$$K_D = \frac{[\bar{B}]}{[B]} \quad \text{and} \quad K_a = \frac{[B]^a}{[\bar{B}]^a} \frac{[A]^b}{[\bar{A}]^b}$$

The relationship can be used in evaluating trace level distribution coefficient. If the ion 'A' is used in large excess and 'B' is at trace level, then

$$K_D = \text{constant} \times \frac{1}{[A]^{b/a}}$$

Or in other words the distribution coefficient of the trace ion B is independent of its concentration for a given solution of gross component. The uptake of the trace ion is thus directly proportional to its concentration in the external solution. It also implies that for ions of equal charge, the distribution coefficient is inversely proportional to the concentration of the eluting ion A provided this concentration is so low that K_a remains essentially constant and that penetration of electrolyte can be neglected (i.e. the outside solution is below 0.5N).

When the ions involved are differently charged, the K_d values will vary with charges of the ions in the eluant solution. Plots of $\log K_d$ against $\log [A]^a$ in case of ions of similar charge will then have a definite slope. But for ions of different charges the slopes of such plots will be different. The ratio of distribution coefficients of two ions can be either unity or more than that. If it is unity then separation possibilities are nil, but if this ratio has a large value, the separation possibilities are there. This ratio can be increased for an exchanger by

involving a suitable complexing agent in the solution phase. The possibilities of separation can also be increased by such a process. But if no complexing agent is present in the solution phase then nature of the exchanger can be modified to show different selectivities for different ions. In other words, presence of an exchanger capable of showing complexation with certain ions can also modify the distribution nature of particular metal ion vis-a-vis a particular exchanger.

4.2 The Present Work

It is now clear that if the distribution data for a large number of metal ions is available for a certain type of exchanger, then the separation possibilities in pairs of two or more ions can be predicted. It is true that distribution data at trace level is much more useful than the data from microlevel studies, yet for applications in industrial problems data macro level is more useful.

In the present work three new exchangers (ZrGAs, ZrSlAs and ZrAAs) have been prepared with organic carboxylic acids as additional ligands in the exchanger. Such exchanger can be expected to show additional selectivities for certain ions. The transition metal ions, thus, can be expected to show greater affinities for such exchangers. In order to ascertain their usefulness for analytical work, cation exchange distribution studies have been carried out here into ions of various types.

Univalent alkali metal ions, trivalent alkaline earth metal ions, transition metal ions of different valency states and a few inner transition metal ions have been taken to study their

distribution on four types of exchangers prepared for this work. All these have been studied at fixed ionic concentrations (macro level) and with fixed quantity of the exchangers. Since it is known that the ionic concentration influences the metal ion distribution, attempts have been made to know the extent to which this happens by studying first the exchange distribution of univalent ions only. They have been studied at ionic concentrations for 0.1M to 0.005M for Li^+ , Na^+ , K^+ , Cs^+ , Ag^+ and Tl^+ ions with all the four exchangers.

The distribution data of the all the other ions, including the above mentioned univalent ions at ionic concentrations $\sim 0.1\text{N}$ have been procured for comparison purposes to show their relative K_d values and show, possibilities of their specific interaction (if any) with the exchangers.

4.3 Experimental

4.3A Reagents and Solutions

In general the chemical used for preparing metal ion solutions were all analytically pure materials for either BDH or E.Merch. Nitrates of lithium, sodium, potassium, rubidium, caesium, ammonium, silver, thallous(I) calcium, strontium, barium, cobalt, nickel, lanthanum(III), cerium(III), uranium(VI) and thorium(IV) were used to prepare their solutions of the required concentration (see tables 4.4.5 to 4.4.8). Only in the cases of magnesium, iron(II), copper(II) and zinc(II) their sulphates were used.

4.3B Titres used

For metal ion distributions both during standardisation of the prepared solutions as well as in distribution studies, titrimetric methods were followed. Disodium EDTA was used for Mg(II), Zn(II), Fe(II), Co(II), La(III), and Th(IV) estimations. Uranium(VI) was estimated gravimetrically as oxinate silver was estimated by using ammonium thiocyanate, while thallous was estimated by potassium iodate. Cerium(III) was estimated with Mohr's salt solution.

Iodometric procedure was adopted for copper(II) as usual.

In case of alkali metals and alkaline earths the extent of exchange was judged by estimating the liberated hydrogen ion from the exchanger after equilibration.

4.3.C Indicators

A variety of indicators were used to suit a particular estimation method.

Their names with specification about their use are given below in the table.

Indicators used in metal ion estimations			
Indicators	Ion for which used	condition	colour change
Erochrome Black T	Zn(II)	pH-10	wine red to blue
Murexide	Ni(II)	pH-10	red violet to blue
Thoron	Co(II)	pH 2-3	red to yellow
Choloroform	Th(IV)	In presence of concentrated HCL 2N	yellow to colourless

Starch	Cu(II)	In presence of KI in acetic acid medium	Blue violet to white
Ferric nitrate	Ag(I)	In presence of nitric acid not more than 20% by volume	Colourless to redish brown
Ferrion	Ce(III)	In presence of conc. H_2SO_4 and Pot. per sulphate	yellow to pink
Pyrocatechol	Mg(II)	In presence of a buffer prepared by mixing 1 vol. of 1 M NH_4Cl and 5 vols. of 1 M NH_4OH	Greenish blue to reddish purple

4.3.D Buffers

A few buffer solutions were required for the adjustment of pH values in metal ion solutions to be estimated by Disodium EDTA titre. These have been given in table below

Buffers Used

pH required	Buffer	Composition	Used in
2-3	2M sodium acetate	2M sodium acetate (272gm in 1 litre)	For the esti- mation of Nickel and Cobalt
10	Ammonium chloride and ammonium hydroxide buffer	67.5gm of NH_4Cl BDH A.R. in 570ml of NH_4OH (sp. gra- vity 0.88) in 1 lt.	Zinc and Magnesium

4.3.E Exchanger

The ~~four~~^{III} exchangers used in these studies were zirconium glutero arsenate, zirconium salicylo arsenate and zirconium adipo arsenate, prepared as per procedures given in chapter II. Always 0.2gm of the exchanger was used in a batch

study.

4.3.F General procedure for distribution studies of metal ions

All metal ion distribution studies were carried out in 150 ml. erlenmeyer flask provided with glass stoppers. In each batch study 20ml electrolyte solution of proper concentration was equilibrated with 0.2gm of the exchanger. The solutions so prepared were stirred intermittently and were left as such for 24 hrs. for attaining complete equilibrium.

After this the aliquots were withdrawn from the supernatant liquid and metal ion estimated in it titrimetrically from the differences in concentration of the metal ions before and after equilibrium studies, the distribution coefficients were calculated as from the relation

$$K_D = \frac{\text{meq. metal in the exchanger per gm.}}{\text{meq. metal in solution per ml of the solution}}$$

The data was procured in this way for alkali metals and Ag^+ and Tl^+ ions at different ionic concentrations. It is reported in tables 4.4.1 to 4.4.4 for all exchangers.

The data for all the ions at one concentrations has been given in tables 4.4.5 to 4.4.8.

4.4 Results

The results have been presented in terms of K_D as weight distribution coefficients with initial ionic concentration in the external solution for Li^+ , Na^+ , K^+ , Cs^+ , Ag^+ and Tl^+ ions on ZrGAs, ZrSlAs and ZrAAs exchangers.

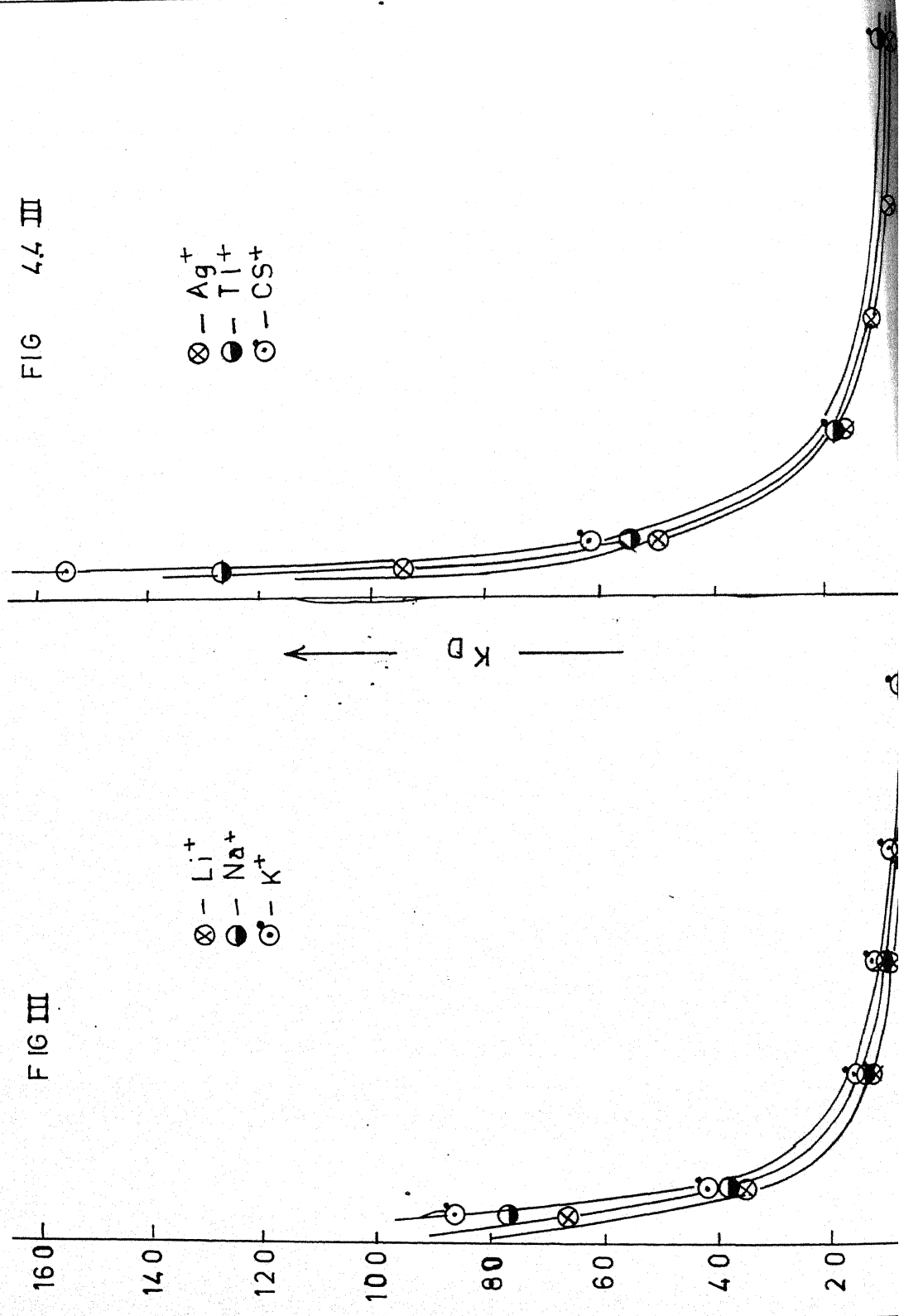
The data presented in these tables have been used to plot graphs for K_D verses ionic concentration in molarity (see figures 4.4 I to 4.4 III).

These plots show very well the progressive increase in K_D with dilution of the external solution.

The distribution data for all the other ions including those reported in earlier tables have been given at fixed ionic concentrations for comparison purpose and showing their relative affinities for the exchangers in tables 4.4.5 to 4.4.8.

Variation of metal ion distribution coefficient (K_d) with ionic loading (or initial ionic concentration of the external solution)

VARIATION OF K_D WITH IONIC CONCENTRATION EXCHANGER USED ZrGAs



VARIATION OF K_D WITH IONIC CONCENTRATION EXCHANGER USED ZrAAs

FIG -4.4 II

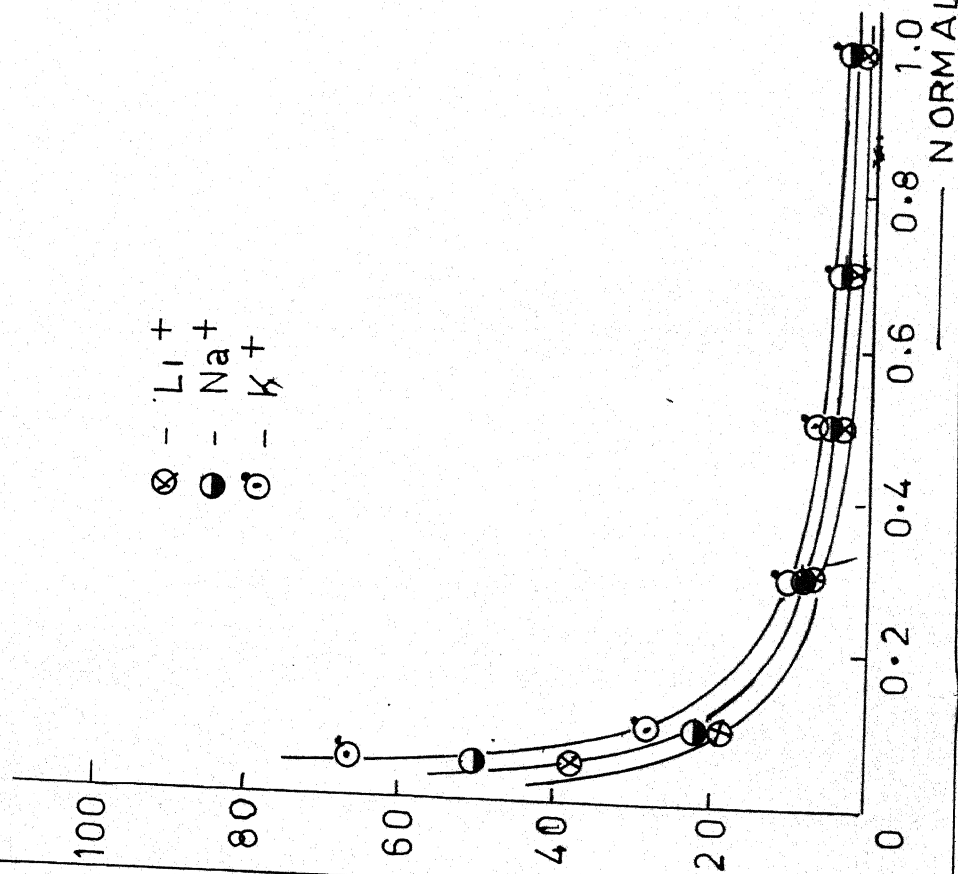
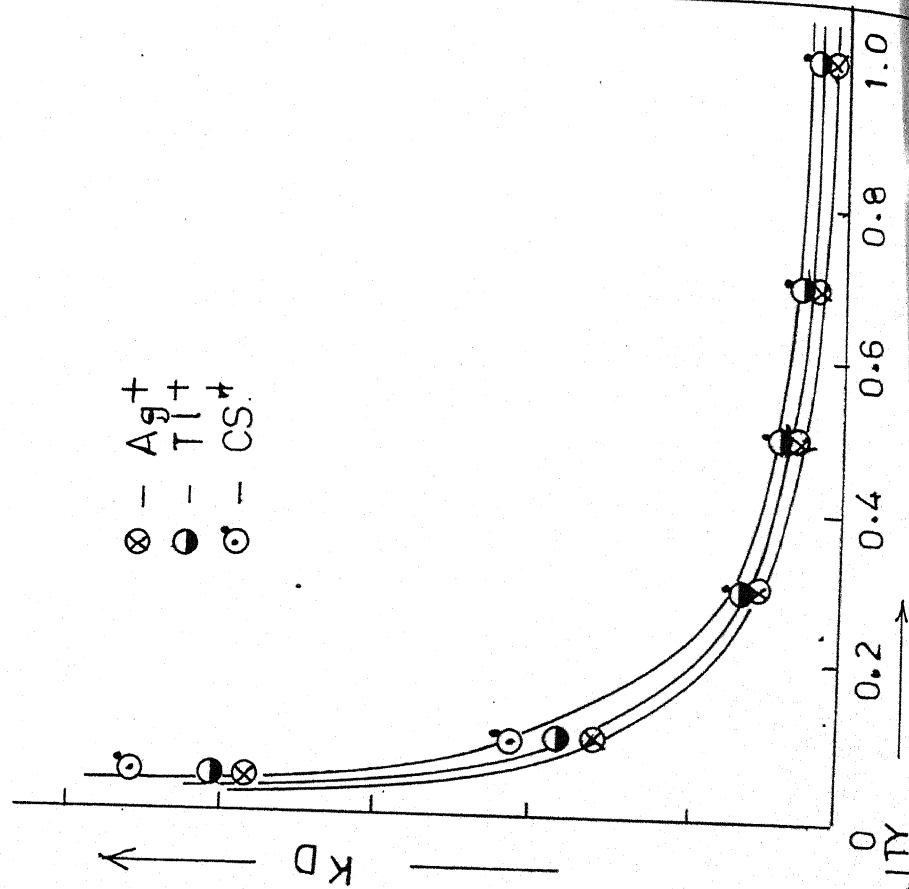


FIG - 4.4 I



VARIATION OF K_D WITH IONIC CONCENTRATION EXCHANGER USED ZrSIAs

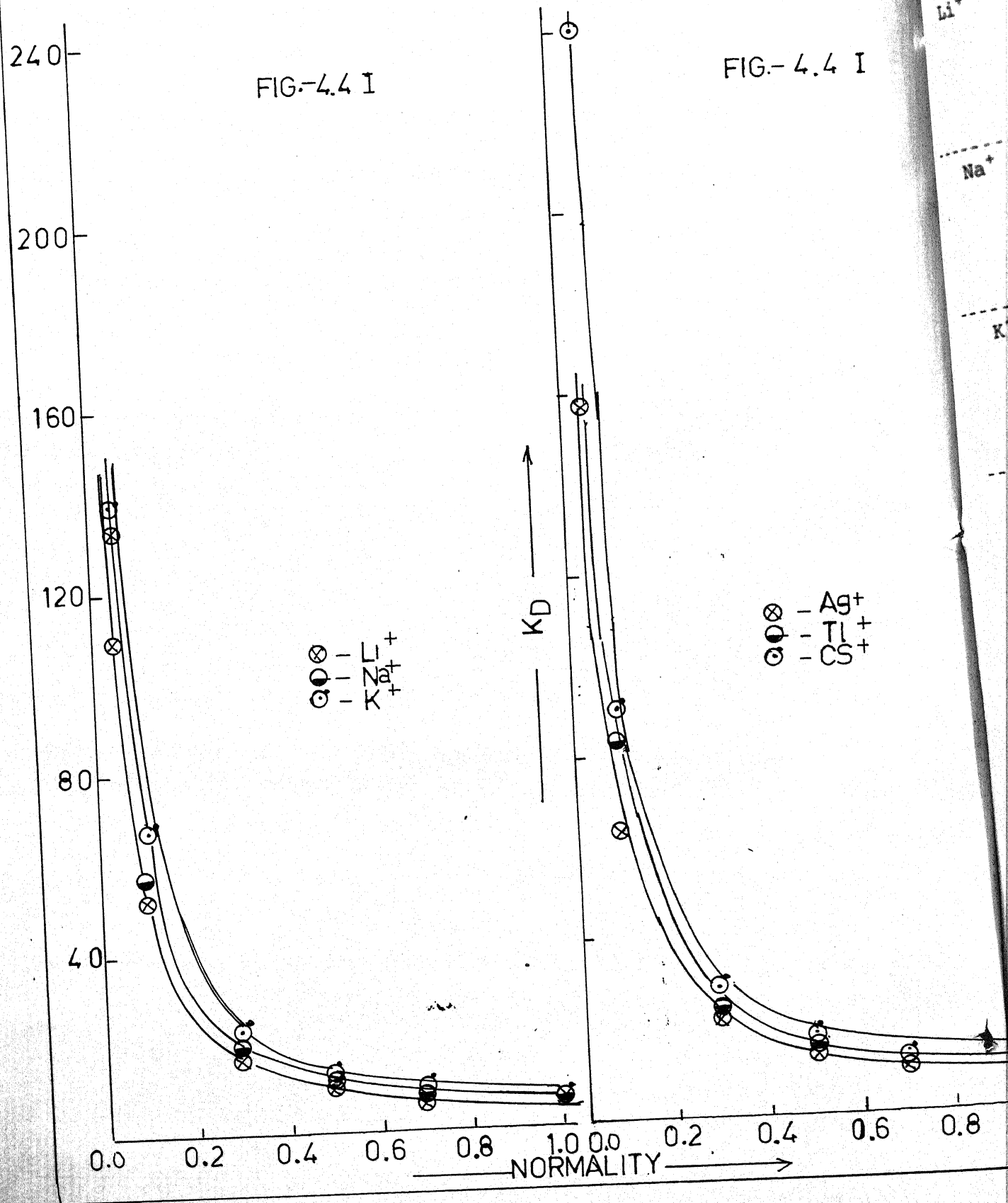


Table - 4.4.1

Exchange of Univalent ion on ZrGAs

Ion exchanged	Exchanger in H^+ form	Ionic Concentration	K_d
Li^+	ZrGAs	0.005	108.12
		0.010	51.68
		0.030	15.92
		0.050	9.20
		0.070	7.01
		0.100	5.10
Na^+	ZrGAs	0.005	130.33
		0.010	56.80
		0.030	17.15
		0.050	10.65
		0.070	7.98
		0.100	5.10
K^+	ZrGAs	0.005	138.42
		0.010	66.66
		0.030	22.22
		0.050	12.76
		0.070	8.96
		0.100	6.18
Cs^+	ZrGAs	0.005	240.50
		0.010	90.69
		0.030	27.10
		0.050	16.07
		0.070	11.40
		0.100	7.86
Ag^+	ZrGAs	0.005	157.14
		0.010	63.15
		0.030	22.22
		0.050	13.67
		0.070	9.50
		0.100	6.60
Tl^+	ZrGAs	0.005	-
		0.010	83.87
		0.030	22.86
		0.050	13.85
		0.070	-
		0.100	7.21

Table - 4.4.2

Exchange of univalent ion on ZrSlAs

Ion exchanged	Exchanger in H ⁺ form	Ionic Concentration	K _d
Li ⁺	ZrSlAs	0.005	66.66
		0.010	35.29
		0.030	12.38
		0.050	8.33
		0.070	5.88
		0.100	4.08
Na ⁺	ZrSlAs	0.005	77.77
		0.010	38.09
		0.030	14.28
		0.050	9.20
		0.070	6.40
		0.100	4.49
K ⁺	ZrSlAs	0.005	85.70
		0.010	42.42
		0.030	14.28
		0.050	9.42
		0.070	6.64
		0.100	4.60
Cs ⁺	ZrSlAs	0.005	155.10
		0.010	61.09
		0.030	19.20
		0.050	-
		0.070	-
		0.100	5.70
Ag ⁺	ZrSlAs	0.005	94.11
		0.010	50.00
		0.030	15.82
		0.050	10.08
		0.070	7.10
		0.100	4.91
Tl ⁺	ZrSlAs	0.005	127.86
		0.010	54.61
		0.030	16.00
		0.050	-
		0.070	-
		0.100	5.1

Table - 4.4.3

Exchange of univalent ion on ZrAAs

Ion exchanged	Exchanger in H^+ form	Ionic Concentration	K_d
Li^+	ZrAAs	0.005	38.09
		0.010	19.78
		0.030	6.89
		0.050	4.49
		0.070	3.19
		0.100	2.22
Na^+	ZrAAs	0.005	50.00
		0.010	22.22
		0.030	8.30
		0.050	4.91
		0.070	3.78
		0.100	2.60
K^+	ZrAAs	0.005	66.66
		0.010	28.57
		0.030	10.52
		0.050	6.10
		0.070	4.37
		0.100	3.00
Cs^+	ZrAAs	0.005	90.60
		0.010	42.30
		0.030	13.00
		0.050	7.77
		0.070	5.49
		0.100	3.81
Ag^+	ZrAAs	0.005	77.80
		0.010	32.55
		0.030	11.26
		0.050	6.60
		0.070	4.70
		0.100	3.20
Tl^+	ZrAAs	0.005	81.13
		0.010	36.96
		0.030	11.55
		0.050	7.10
		0.070	5.26
		0.100	3.60

Comparative Cation exchange distribution data for different ions
on ZrGAs at fixed ionic concentration

Table - 4.4.5

Metal ion	Molarity of solution	K_d
Li^+	0.100 M	4.98
Na^+	0.100 M	5.68
K^+	0.100 M	6.00
Rb^+	0.100 M	6.90
Cs^+	0.100 M	8.32
NH_4^+	0.100 M	6.15
Ag^+	0.100 M	6.54
Tl^+	0.100 M	7.30
Ca^{++}	0.100 M	3.96
Sr^{++}	0.100 M	4.45
Ba^{++}	0.100 M	15.84
Cu^{++}	0.100 M	4.18
Mg^{++}	0.089 M	3.50
Zn^{++}	0.088 M	3.80
Fe^{++}	0.088 M	13.00
Co^{++}	0.079 M	6.86
Ni^{++}	0.085 M	4.00
La^{+++}	0.086 M	10.20
Ce^{+++}	0.430 M	5.58
Th^{++++}	0.120 M	32.80
U^{+6}	0.087 M	6.68

Comparative Cation exchange distribution data for different ion
on ZrSILAs at fixed ionic concentration

Table - 4.4.6

Metal ion	Molarity of solution	K_d
Li ⁺	0.100 M	3.80
Na ⁺	0.100 M	4.00
K ⁺	0.100 M	4.00
Rb ⁺	0.100 M	5.34
Cs ⁺	0.100 M	5.06
NH ₄ ⁺	0.100 M	4.80
Ag ⁺	0.100 M	4.90
Tl ⁺	0.100 M	5.10
Ca ⁺⁺	0.100 M	3.00
Sr ⁺⁺	0.100 M	5.00
Ba ⁺⁺	0.100 M	10.80
Cu ⁺⁺	0.100 M	6.40
Mg ⁺⁺	0.089 M	3.00
Zn ⁺⁺	0.088 M	4.50
Fe ⁺⁺	0.088 M	11.50
Co ⁺⁺	0.079 M	5.64
Ni ⁺⁺	0.085 M	3.00
La ⁺⁺⁺	0.086 M	7.50
Ce ⁺⁺⁺	0.430 M	2.90
Th ⁺⁺⁺⁺	0.120 M	21.00
U ⁺⁶	0.087 M	5.00

Comparative Cation exchange distribution data for different ion
on ZrAAs at fixed ionic concentration

Table - 4.4.7

Metal ion	Molarity of solution	K_d
Li ⁺	0.100 M	1.88
Na ⁺	0.100 M	3.00
K ⁺	0.100 M	3.04
Rb ⁺	0.100 M	3.50
Cs ⁺	0.100 M	3.70
NH ₄ ⁺	0.100 M	3.00
Ag ⁺	0.100 M	3.75
Tl ⁺	0.100 M	3.50
Ca ⁺⁺	0.100 M	5.00
Sr ⁺⁺	0.100 M	5.40
Ba ⁺⁺	0.100 M	8.00
Cu ⁺⁺	0.100 M	7.50
Mg ⁺⁺	0.089 M	4.80
Zn ⁺⁺	0.088 M	2.50
Fe ⁺⁺	0.088 M	4.80
Co ⁺⁺	0.079 M	2.00
Ni ⁺⁺	0.085 M	2.50
* La ⁺⁺⁺	0.086 M	-
Ce ⁺⁺⁺	0.430 M	2.36
Th ⁺⁺⁺⁺	0.120 M	15.00
U ⁺⁶	0.087 M	3.80

Discussion

The true measure of affinity of an ion is the thermodynamic equilibrium constant which is independent of the total ionic concentration in an equilibrium study. But this is not so for the so called selectivity coefficient (K_a). This term is dependent on the ionic loading of the resin. Thus K_a is a function exchanger composition at equilibrium variability of K_a therefore makes it difficult to use this term as a measure of relative exchange of different ions in a definite set of condition. Moreover, it is defined in terms of concentrations of counter ions in the solution and exchanger phases using law of mass action applied strictly stoichiometric exchange process.

Many a times the total uptake of an ion is the result of not only the true exchange but also the processes other than it, like ion association and complex formation in the resin phase. In such cases the evaluation of K_a does not provide the true picture or the values may be deceptive. For such reasons the comparative uptake of ions by an exchanger is measured in terms of their distribution coefficient, K_D which gives the total absorption of the ions by an exchanger by any of the above mentioned processes. These values are therefore more useful in analytical work where total uptake of an ion is important rather than its exchange.

The results of metal ion distribution of common normal and transition metal ions together with some inner transition metal ions on the newly prepared exchangers have been obtained in this study to have a comparative idea of their total uptake under similar conditions. But at the same time effect of total ionic

concentration of the external solution on this uptake has also not been overlooked.

The distribution of the metal ion is inversely proportional to the concentration of the solution, because

$$K_D = \frac{[\bar{B}^+]}{[B^+]}$$

$$K_a = \frac{[\bar{B}^+]}{[B^+]} \frac{[A^+]}{[\bar{A}^+]}$$

$$\text{or} = \frac{[\bar{B}^+]}{[B^+]} \frac{(C_o - [B^+])}{(q_o - [\bar{B}^+])}$$

$$\text{or} = \frac{[\bar{B}^+]}{[B^+]} \frac{(C_o - [B^+])}{(q_o - [\bar{B}^+])}$$

If B^+ is tracer component then

$$K_a \approx K_D \cdot \frac{C_o}{q_o}$$

$$\text{or } K_D \approx K_a \cdot \frac{q_o}{C_o}$$

Here q_o = total number of meq of exchangeable cations per gm. of the resin (or its saturation capacity) and C_o is the concentration of the initial solution (meq per ml). Since q_o is constant and K_a is also apparently constant, hence

$$K_D \propto \frac{1}{C_o}$$

In other words K_D becomes more with decreasing concentration of the solution. To test this attempts were first made to study the uptake of univalent metal ions from alkali metals, thallium(I) and silver(I) to get their K_D values at

solution concentration from 0.1 N to 0.005 N. The data have been presented in tables 4.4.1 to 4.4.3 for all three exchangers, namely ZrGAs, ZrSlAs and ZrAAs.

The K_D values for these ions have shown a sharp increase in the metal ion uptake with decreasing metal ion concentration in the solution. Plots of K_D verses solution normality for Li^+ , Na^+ , K^+ , Ag^+ , Tl^+ , and Cs^+ ions have been given in figures 4.4.I for exchange on ZrGAs. These plots are not linear, but are very steep showing very high K_D values at low concentrations. But this increase is ~30 times for Cs^+ ion, showing exceptional exchange behaviour for this ion.

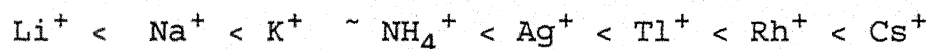
In cases of ZrSlAs and ZrAAs the trends of the plots of K_D verses normality were the same (see plots in figures 4.4.II-III). But comparatively these exchangers gave lesser exchange of all ions than ZrGAs. This is naturally because of the good exchange properties of ZrGAs. The Cs^+ ion has shown greater uptake than all other ions in all cases.

In no case K_D was varying linearly with solution concentration this is contrary to the general belief based on the derivation given above for tracer level concentrations of the exchanging ion. For macro-level concentrations (0.1 N to 0.005 N) though K_D increases with decreasing solution concentration, alright, but this change is not linear.

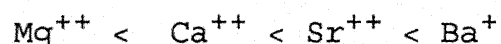
It is therefore essential to study the comparative uptake under identical or nearly similar conditions to have an idea about separation possibilities of different types of ions. As many as twenty one ions have been compared for their relative uptake by ZrGAs (table 4.4.5), ZrSlAs (table 4.4.6) and ZrAAs (table

4.4.7) at concentration $\sim 0.1N$). The weight distribution coefficient values reported in these tables show that the sequence of increasing uptake for different type of ions is more or less the same as expected from their decreasing sequence of hydrated ionic sizes.

Thus for univalent ions it is



For ions from alkaline earths it is

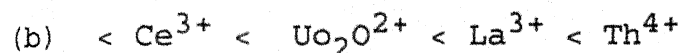
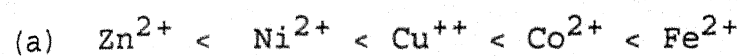


However the values for Ba^{++} were quite high, being 16.2 in ZrGAs 10.6 for ZrSlAs and 8.2 for ZrAAs. These values are four times that of Sr^{++} in the case of ZrGAs exchanger and practically double than those for Sr^{++} in other exchangers. This shows clearly for the exceptional behaviour of Ba^{++} ion for which ZrGAs may be considered to be a selective exchanger.

Similar relative affinities for uni and divalent ions have been shown for the ZrP gels for trace studies by different workers(3,4,5,6).

In clay minerals too the same sequence for alkali metals have been shown by Schacrtschabel(7). Though in zeolites the ionic sieve properties arise due to their channel diameters which are too small to permit passage of certain cations(as Cs^+), yet with the structure with more open network, this consideration becomes unnecessary. So in fanjasite, the extent of exchange among the alkaline earths increases in the order $Mg^{++} < Ca^{++} < Sr^{++} < Ba^+$ suggesting the involvement of hydrated ions(8). On hydrous $MnO(OH)_2$ also the well defined sequence of affinity as per hydrated ionic sizes has been observed(9).

For transition and inner transition metal ions the sequences of up take were as below.



The exchanger ZrSAs has shown again high K_D for Fe^{2+} , La^{3+} and very high K_D for Th^{4+} . Thorium(IV) uptake has been the highest in all the exchangers. Its K_D has been about 6 times than uranium (VI) in ZrGAs exchanger. Naturally by using suitable initial solution concentrations the possibilities of the separation of thorium(IV) from cerium(III) or uranium(VI) can be predicted by using the new exchanger zirconium Glutero Arsenate. This exchanger is expected to prove a very selective material for thorium uptake and hence for its separation from a mixture of other ions.

Amongst the common transition metal ions it can be utilised for Iron(III) uptake and its separation from other ions such as Zn(II), Ni(II) and Cu(II) which are common metal found in alloys with iron.

This high uptake of Fe(III) appear to be due to the presence of additional succinate ligand in the exchanger ZrSAs matrix which is capable of complexing with iron quite strongly. The K_D falls down in other exchangers in the order $\text{ZrSlAs} > \text{ZrAAs}$ showing lesser complex stabilities for Iron and glutarate, adipate and salicylo ligands.

For separation purposes the initial ionic concentrations that may be prepared should be much below 0.1 N at which these values have been reported. Since at least 10 fold

difference in K_D is desirable for planning separations, lower ionic concentrations of exchanging solutions is desired. The studies with univalent metal ions (tables 4.4.1 to 4.4.3) show that by going up to 0.005 N values can be increased up to ~ 20 times. Hence any concentration from ~0.001 to 0.005 N may be useful in attempting separations with these exchangers.

The comparative usefulness of ZrGAs is evident from higher K_D values for any particular ion in it as compared to those in ZrSlAs or ZrAAs.

Limitation of time prevented us from proving this with actual examples of separation to justify this.

4.6 References

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CHAPTER - F I V E

5.1 Introduction

5.2 Earlier studies on Zirconium phosphates gels and crystals

- 5.2 (A) Thermogravimetry
- (B) Infrared studies

5.3 The work reported in this chapter

5.4 Estimation of carbon in the newly prepared exchangers

- (A) Conclusions

5.5 Infrared studies of newly prepared exchangers

- (A) General
- (B) Experimental and results
- (C) Discussion and conclusions

5.6 Thermal analysis of ZrGAs, ZrSlAs and ZrAAs.

- (A) General
- (B) Earlier work on zirconium based exchangers.
- (C) Experimental
- (D) Discussion and conclusions

5.7 References

*Studies on the structure of newly prepared exchanger***5.1 Introduction**

As has been mentioned in the earlier chapters (ch. one) that the precipitate of inorganic ion exchangers such as zirconium phosphate or other zirconium based exchangers range from gels of amorphous nature to well defined crystalline products. It is possible to obtain compounds crystallinity intermediate between those of the gels and the crystalline products. These have been termed semi-crystalline products. The structural studies of such compounds have been done by the variety of different angles throwing light on their building up units, crystalline and non crystalline nature stability and hydrolytic behaviour. Since all these aspects cannot be studied by a single technique. Attempts have been made to study the problem by using different techniques.

5.2 Earlier studies on zirconium phosphate gels and crystals**5.2.a Thermogravimetry**

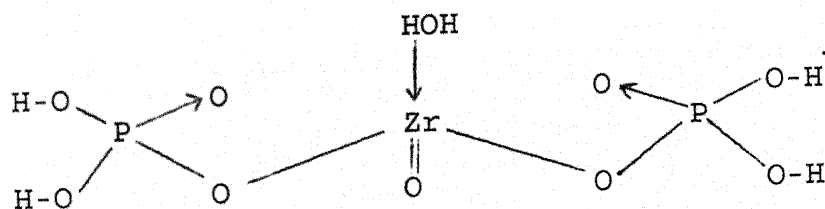
The structural studies using thermogravimetric analysis had been of much use in deciding the initial intermediate and final forms of the products and suggest various possible phase changes during heating of the samples to high temperatures.

Thermogravimetry had been particularly useful in deciding various phases during the heating of the prepared material from, say 100°C through above a thousand degrees when amorphous or poorly crystalline material were used.

As is known gels result from the rapid mixing of a

soluble Zr(N) salt with phosphoric acid or a soluble phosphate.

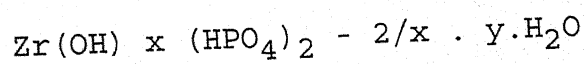
The materials prepared with a P-Zr ratio as two were shown by De-Boer as a non hydrogen phosphate $\text{Zr}(\text{HPO}_4)_2$. But blue methonal and others³ did not agree with that and suggested the possibility of zirconyl compound as $\text{ZrO}(\text{H}_2\text{PO}_4)_2$.



The thermogravimetry of these compounds in P-Zr ratio of two showed loss of one water molecule at 100-135°C and a second at 240-350°C. But when heated to 700° it give a poorly crystalline pyrophosphate furhter heating to 900° and annealing improved the crystallinity of the products. The original product was given the the composition $\text{ZrO}_2, \text{P}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ or $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$.

Similarly when crystalline product. is prepared by refluxing the gel with phospheric acid to give the so called α -ZrP, the thermogrametric analysis has provided much useful data. The material loses one water molecule at 80-120°C and the second molecule is lost at 300-650°C. Finally at 700-750°C it gets converted to pyrophosphate. Hence again the composition $\text{ZrO}_2, \text{P}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ or $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ was confirmed.

Thus the gels and crystals were shown to have the same chemical composition corresponding to the P-Zr ratio of two 4,5.6 when this ratio was less two, the phosphate groups were shown to be present as monohydrogen phosphate. The general formula of gels can be written as

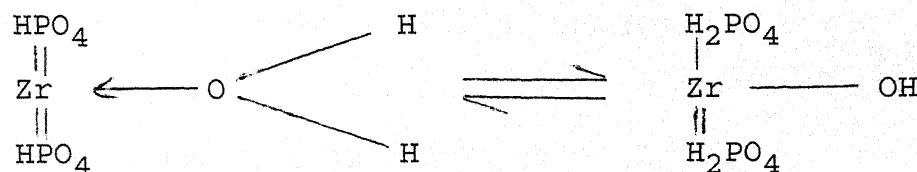


where x varies from 0 to 2 and the exact value of y depends on the method of drying. This general formula also suggested the exchange capacity to be corresponding to two hydrogens from the monohydrogen phosphate group⁸. Hence the exchange of protons from hydroxyl groups is expected to be negligible.

5.2.b Infra red studies on Zirconium phosphate

Four independent studies have been made by Clearfield⁹, Vedely et al.¹², Mourier et al.¹³ and Dearbrilges¹⁴. But these studies have been carried out with α -ZrP which is a crystalline product. Attempts have been made in these studies to elucidate particularly the hydrogen bonding scheme in α -ZrP. There are four bands in OH stretching region corresponding to the fact that there are four OH groups in α -ZrP.

Mounier and Winanad¹³ have assigned a peak at 3150cm^{-1} to water coordinated to zirconium and a peak at 3150cm^{-1} to water coordinated to zirconium and a peak at 3510cm^{-1} or 3590cm^{-1} to a hydroxyl group attached to zirconium and hence they have suggested two tautomeric forms (a) and (b) for crystalline zirconium phosphate.



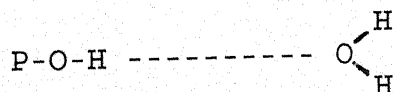
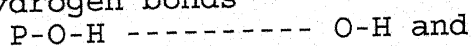
Presence of two sharp peaks at 3670cm^{-1} and 3610cm^{-1} for OH^{-1} groups of basic character support this inference the peak at 3510cm^{-1} implies a strong bonding of zeolite water.

The findings of Dearbridges¹⁴ suggest that the bands at 3150cm^{-1} and 3320cm^{-1} are due to OH^{-1} stretch of interselital

water. A band at 1620cm^{-1} is due to the bonding mode of OH groups.

The peaks at 3590 and 3510cm^{-1} are attributed to the OH stretch of the acidic phosphate groups. The fact that two peaks do not coincide was taken as an indicator that the two monohydrogen phosphate groups differ in acidity.

Vesely et al ¹² have given their conclusions regarding IR of α -ZrP more or less in a similar way as Dearbridges. Further they have shown symetric and antisymetric stretching vibrations for the phosphate group in the region $950-1180\text{cm}^{-1}$. These as well as one band at 1250cm^{-1} are due to P-O vibrations. The bands at 3150cm^{-1} and 3300cm^{-1} have been attributed in this study also to strong H-bond from the water-hydroxyl groups to the 3590cm^{-1} are due to ong hydrogen bonds



when the α -ZrP compound is equilibrated with D_2O then the new peaksd appear at 2450cm^{-1} (due to denterated spectrum). The original peaks at 3150cm^{-1} and denterated at 3300cm^{-1} are alsao shown in this spectrum as two distinct peaks at 3150cm^{-1} and 3290cm^{-1} . But the portions of 3510cm^{-1} and 3590cm^{-1} remain fixed.

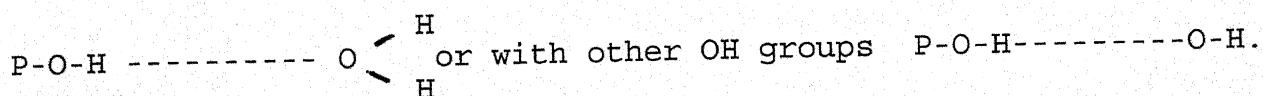
These latedpeaks were due to phosphates groups which are held together rigidly in these crystals. The peaks at 3150cm^{-1} and 3300cm^{-1} appear therefore to originate from the water molecules present in the crystalline compound.

The above studies are still not completely definite ofcourse they are qualitative agreement with the certain

features of the crystal structure. However, it is less certain that the bands at 3150cm^{-1} and 3300cm^{-1} represent strong hydrogen bond: where as the very sharp bands at higher frequencies represent the weaker bonds. I.R. evidence points out that stronger H-bonds originate with the water molecule hydrogens as donars.

The structure of amorphous ZrP gels is sufficiently disordered. It has been shown by Clearfield and Stynes⁴ that I.R. patterns of such gels possess only one broad band in the -OH stretch region as compared to four in crystals¹³. Thus the gel P-OH group and expected to possess broad range of acidities.

The I.R. spectrum thus provides evidence only for the existance of co-ordinated water and possibilities of H-bonding with OH group of the acidic phospahte with coordinated water as



It may also give bands or peaks for P-O and Zr-O stretching and bonding modes. Still the I.R. studies are sufficiently speculative and offer little by way of help to structure determination of such compounds.

5.3 The work reported in this chapter

From the above details about different approaches to elucidate the structure of ZrP crystals or gels it is definite that no simple technique can provide the complete picture, even after attacking the problem from different angles, the results are more speculative rather than definitive. Still when one prepares newer exchnagres with the same base it is advisable to

try all possible aids to arrive at conclusions regarding the structure of such materials.

In addition to α -ZrP, the corresponding titanium phosphate designated as α -TiP and zirconium-arsenate designated as α -ZrAs have the same structure ^{32, 33} unit cell dimension of these compounds are very close to each other.

Since the compounds prepared by workers were all based on zirconium phosphate. Attempts have been made to throw light on their structural simlavitng with pure ZrP gels. Any differences due to the incorporation of organic carboxylic compounds have been adequately made clear from such studies. The new compounds thus have been carefully examined to put forth their expected structures in their part of the work.

The three new inorganic exchangers have been prepared to that used in the preparation of ZrP. Whether the organic part has been effectively incorporated in this arrangement during the preparative steps was furhter proved by the estimation of cenbon content of the compound. The expected composition were confirmed on the basis of carbon determination in all the prepared compounds.

The proof of their similarity in structure with amorphous zirconium phosphate gels has been provided with I.R. spectral studies. These studies have also been done to prove that the newer compounds have additional COOH groups in them provided by the incorporation of organic acids into the structure of ZrAs within is similar to ZrP.

Lastely detailed thermo-analysis have been reported to show how the loss of water takes place in the newer compounds and

how these compounds undergo decomposition by heating up to 800° to 1000°C . The weight loss studies using a self recording thermobalance have been performed with all the new exchangers ie. ZrGAs, ZrSlAs and ZrAAs. These studies have helped in arriving at the final composition of these preproducts before heating, during heating and after heating.

5.4 Estimation carbon in the newly prepared exchangers

The compounds prepared were expected to contain additional functional groups due to incorporation of Gluteric, salicylic and Adibic acids during the methods of preparation adopted for zirconium arsenate. Thus zirconium-glutero-arsenate and zirconium salicyl-arsenate and zirconium-adipo-arsenate were expected to be prepared. It was thought as first supposition that these acids entered the matrix of zirconium-arsenate polymer by coordinated to Zr-atoms by the use their acidic hydrogen of carboxylic groups. Hence the percentage of carbon expected with different possible ratios of ZrO_2 acid; As_2O_5 were calculated counduring these to be 1:1:1 or 1:0.5:1 on molecular ratio basis.

All the three prepared samples were used to estimate carbon by standard semi micro methods and the results as percentage of carbon in the compounds have been reported in table 5.4.1 for all the compounds. The theoretical percentage for the ratios 1:1:1 and 1:0.5:1 were similar with the experimentally obtained values to arrive at final conclusions given in the table.

Thus it was found that the ZrO_2 : Organic acid : As_2O_5 ratio was 1:0.5:1 for ZrGAs and ZrSlAs it was 1:1:1 for ZrAAs.

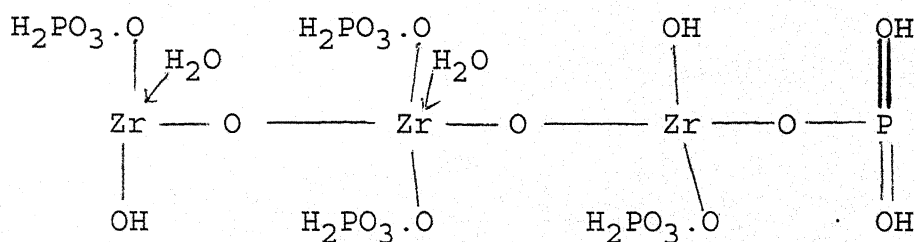
Estimation of carbon in the newly prepared exchangers

Table 5.4.1

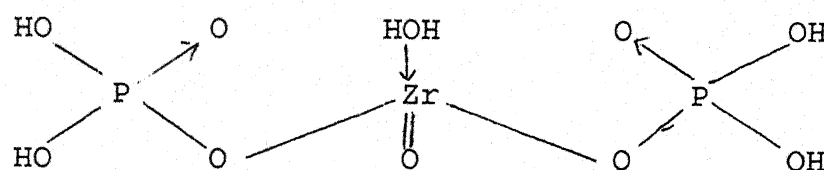
Exchanger	Carbon estimated %	Carbon expected theoretically in the compound for the $\text{ZrO}_2:\text{Org acid}:\text{As}_2\text{O}_5$ ratios		Therefore expected $\text{ZrO}_2 : \text{Org acid}$
		1:0.5:1	1:1:1	
ZrGAs (heated below 100°)	7.30	7.40	14.80	1:0.5:1
ZrSlAs (heated to 100°)	16.00	8.90	18.00	1:1:1
ZrAAs (heated to 100°)	9.09	8.70	17.40	1:0.5:1

5.4 a Conclusion

A compound with a ratio of $\text{ZrO}_2 : \text{P}_2\text{O}_5$ as 1:1 or $\text{Zr}:\text{PO}_4$ ratio as 1:2 was prepared by Baetale and Pelsemakers²⁶ was prepared and they suggested the structure of alternate zirconium oxygen chain with coordinated water to zirconium atoms as below. It contained two H_2PO_4 groups per zirconium atom justifying Zr to PO_4 ratios as 1:2.



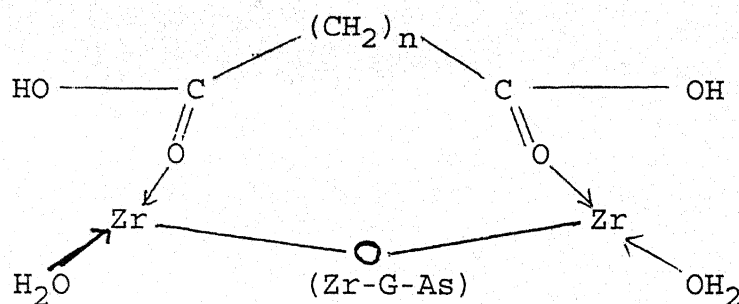
However, DeBoer suggested a monohydrogen phosphate $\text{Zr}(\text{HPO}_4)_2$ under such conditions of P:Zr ratio of 2. But formation of $\text{ZrO}(\text{H}_2\text{PO}_4)_2$ under similar conditions has also not been ruled out^{2,3}. Bluemethonal^{2s} has suggested



Structure for this zirconyl compound. Since both these compounds differ only in additional oxygen and two H_2PO_4 in the Bluemethonals formula rather than two HPO_4 groups in De-Boer's structure.

Since zirconium arsenate has a structure similar to zirconium phosphate so the newer compounds $\{\text{ZrGAs}\}$, ZrSlAs and ZrAAs may be expected to retain either of the two possible basic structural arrangements for Zr and AsO_4 in their structures which may be finalised on the basis of wt loss studies as done in the case of simple ZrP by Clearfield et al⁴ and Ahrlund et al^{5,6}.

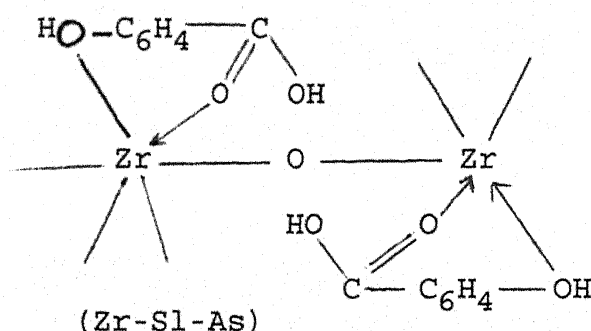
This ration studies for organic acid part in the new exchangers suggests the involvement of one molecule of the organic ligand between two Zr-atoms possibly by coordinate at the two zirconium in the Zr-O-Zr chain as below



so that now per zirconium atom it is only 0.5 mole ratio of the organic acid involved in Zr-G-As and ZrAAs .

In Zr-Sl-As in the situation is slightly different as the compound has salicylic acid has only one COOH group and one OH group in ortho position. The coordinated groups are two again but both newer to each other (ortho to each other) coordinated to the

same Zr-atom in the Zr-O-Zr chain expected linkages in Zr-Sl-As may be as below



The Zr:org acid : As ratio of 1:1:1 can then be justified.

The above justification on the basis of other data such as that from I.R. given in other sections that follow now.

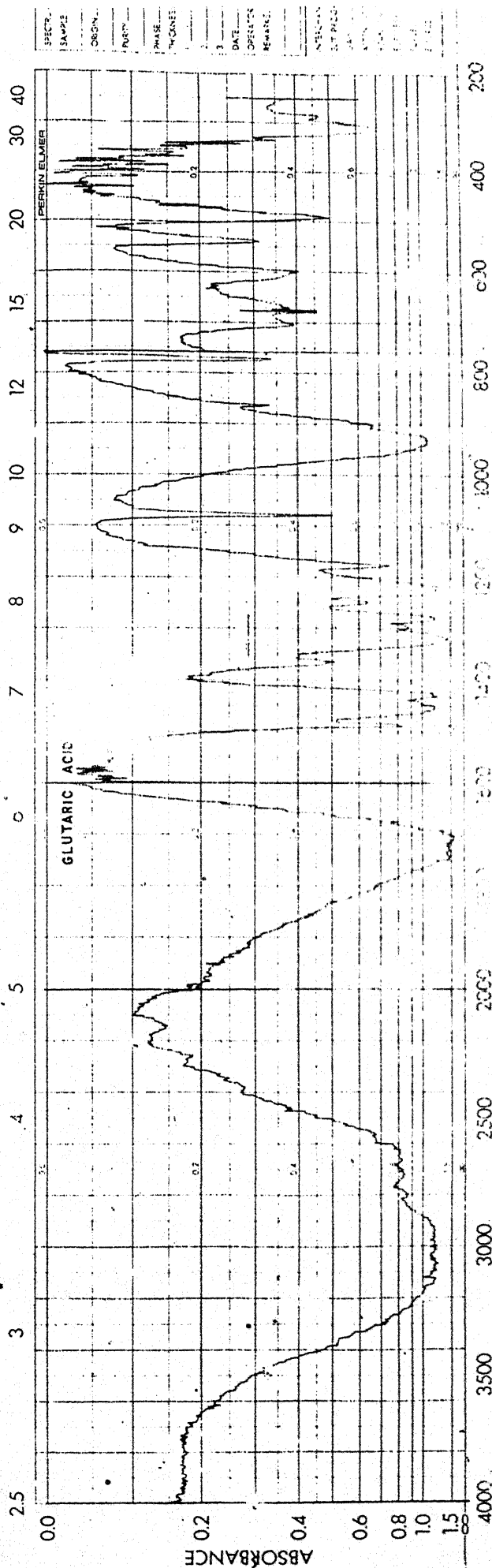
5.5 Infrared studies of newly prepared exchangers

5.5(a) General

It has been indicated in the introductory remarks on IR studies of zirconium based exchangers that the characteristic bands in the region $3510-3590\text{ cm}^{-1}$ and $3300-3350\text{ cm}^{-1}$ are characteristic of -OH groups of different nature (basic, water and acidic) in the compounds and have been observed by all the investigators^{12, 13, 14} the band at 3150 cm^{-1} is particularly showing coordinated water to zirconium atom several bands within the region $965-1250\text{ cm}^{-1}$ have been shown for As-O vibrational modes while a few bands at lower frequency side i.e. < 530 , have been shown for Zr-O vibrational modes and AsO_2S modes (at $600, 530, 415, 400, 375\text{ cm}^{-1}$).

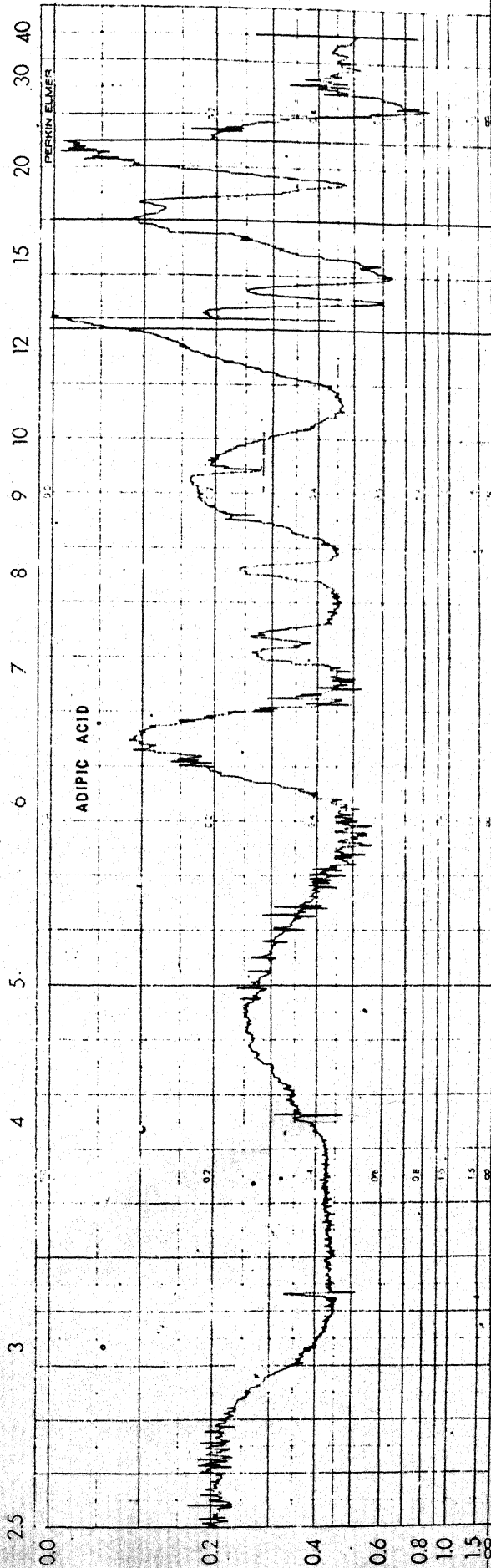
All these characteristic frequencies in crystalline zirconium based exchangers are not found in amorphous structures. The gels show only one broad band in the OH stretch region rather than the four in the crystalline products. The arsenate groups in

WAVELENGTH MICRONS



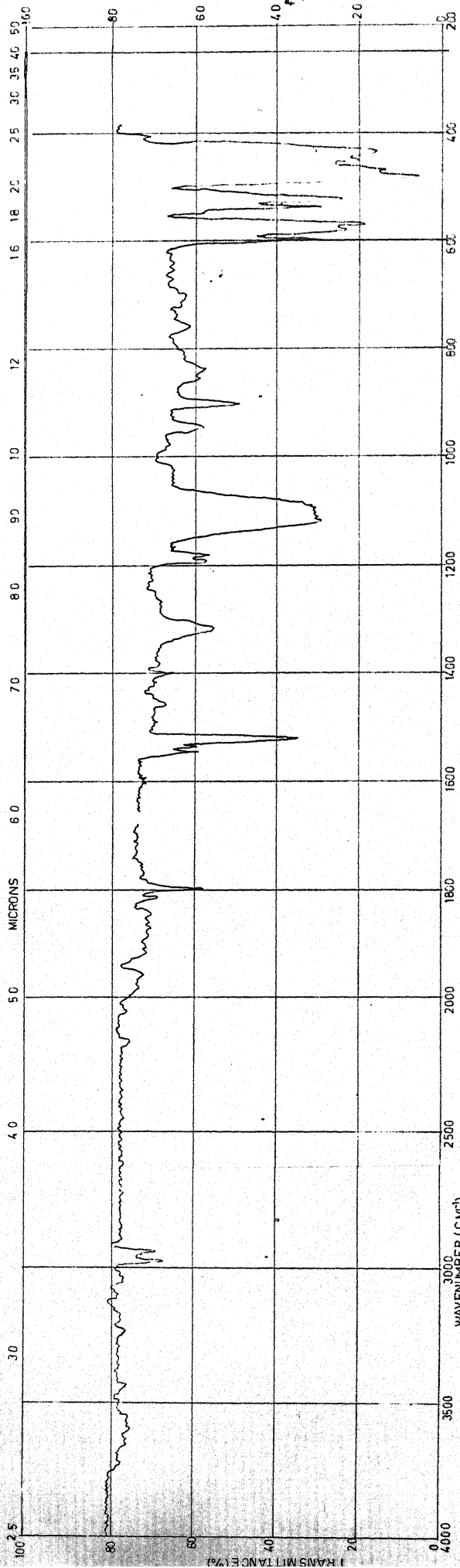
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 ORIGIN _____
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 NAME _____
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 ANALYST _____
 DATE _____
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WAVELENGTH MICRONS



SPECTRUM NO.	
SAMPLE	
ORIGIN	
PURITY	
PHASE	
THICKNESS	
1	
2	
3	
DATE	
OPERATOR	
REMARKS	
INTERCHANGE	
SLOT PROGRAM	
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SCALE	
SOURCE CURRENT	

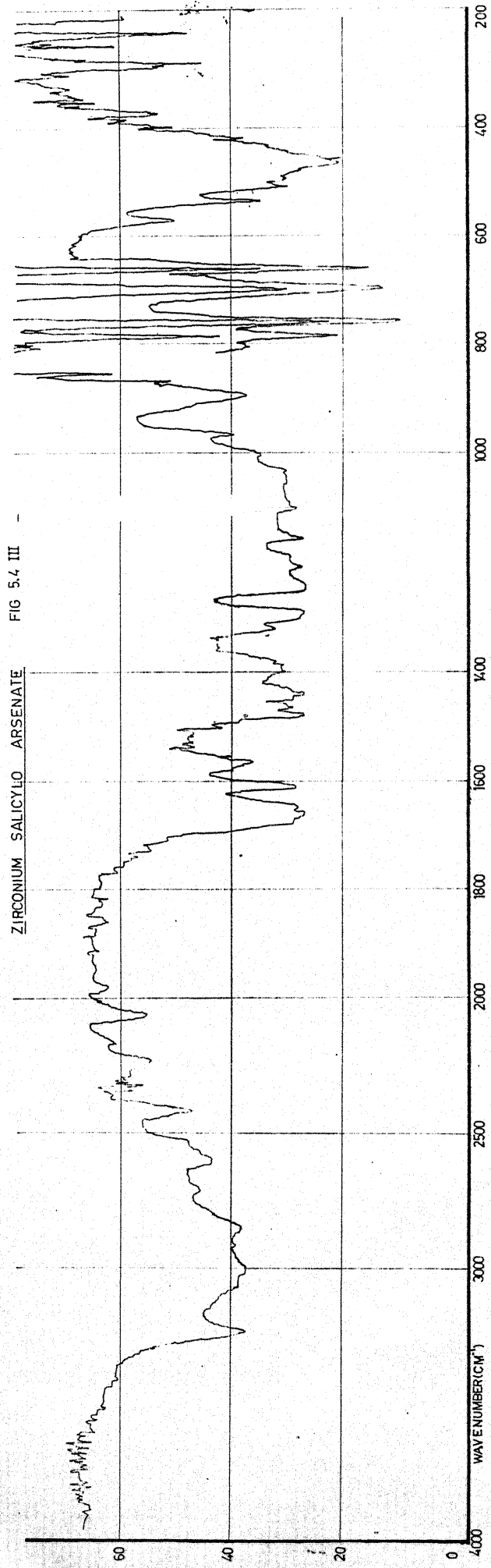
ZRCONIUM ADIPO ARSENATE 5.4 IV



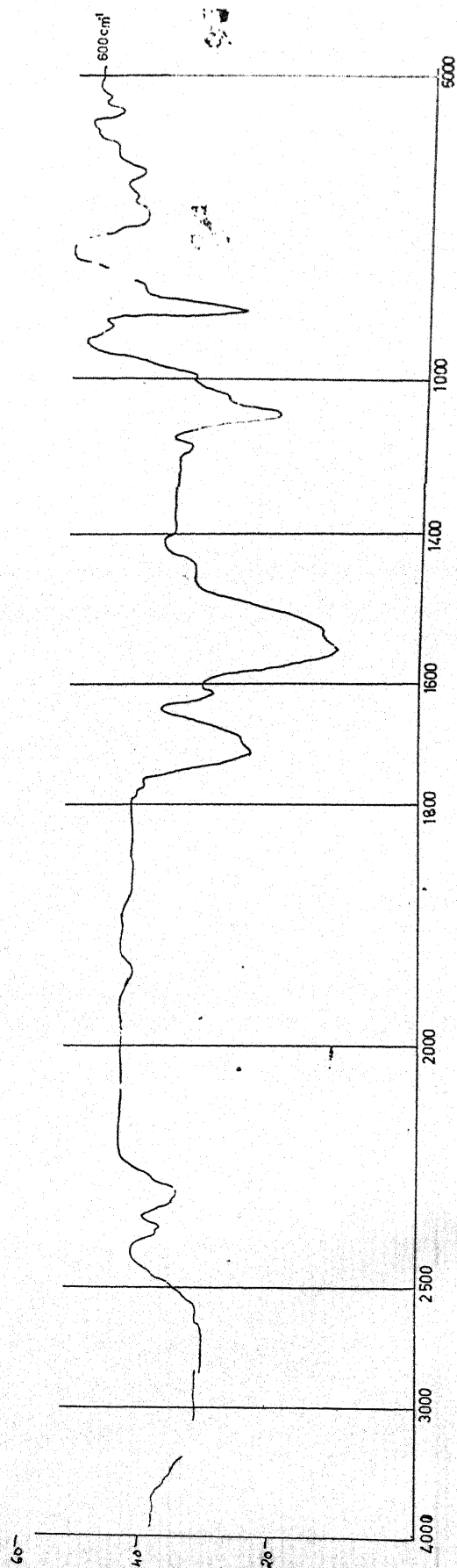
SAMPLE	ORIGIN	REMARKS	SCAN MODE		OPERATOR
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SOLVENT _____ CONCENTRATION _____ CELL PATH _____					

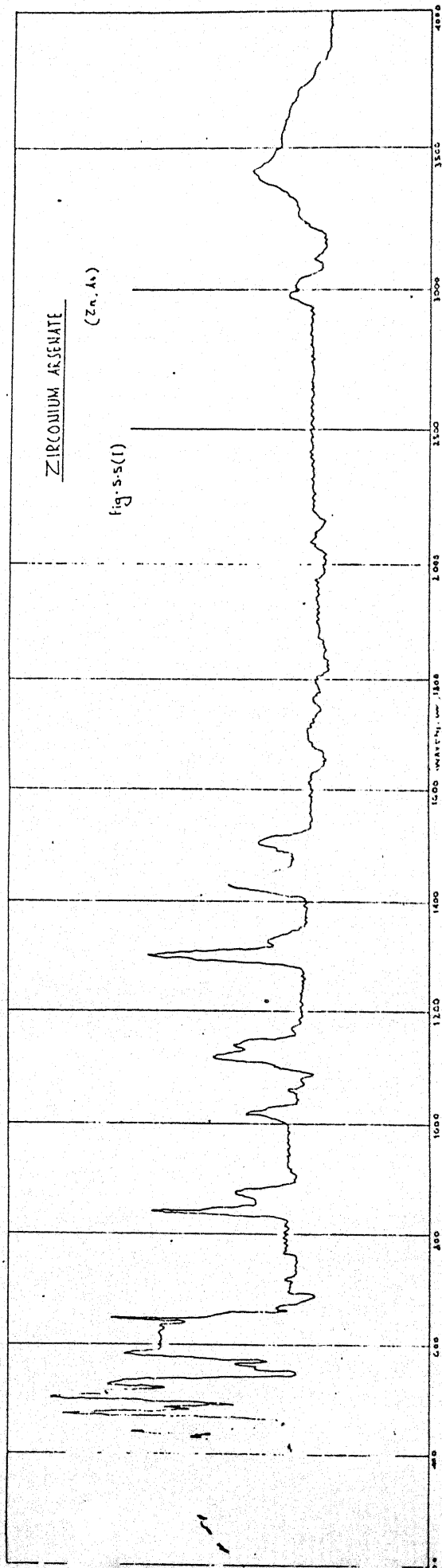
ZIRCONIUM SALICYLO ARSENATE

FIG 5.4 III



ZIRCONIUM GLUTERO ARSENATE FIG 5.4 II





the gels are partly in a highly strained configuration and partly in the regular arrangement in the crystal.

No detailed IR studies have been provided amorphous zirconim based gels but on the basis of the assumption that the amorphous structure results from the disorderly aggregates of small crystallites, it is possible to assign tentatively the observed bands in the IR - spectra of prepared gels of any type. Attempts, therefore have been made in this section to interpret the observed IR-behaviour the newly prepared compound (ZrGAs, ZrSlAs and ZrAAs) in comparision to simple ZrAs prepared under similar conditions.

It is further essential to study IR-spectra in the present case of compound because they are expected to contain extra ligands in their structure derive from the organic acids used in their synthesis.

5.5 b Experimental and results

The IR spectral studies have been carried out by using Perkin-Elmer IR-spectra photometer, model 541.

Fig 5.5.I gives the IR spectra of pure ZrAs prepared under our conditions or preparing ZrGAs, ZrSlAs and ZrAAs. The figures 5.5 II to 5.5 IV show the IR spectra of the prepared compounds namely zirconium-glutero-arsenate and zirconium salicyl-arsenate and zirconium-adipo-arsenate respectively.

On the basis of these IR-spectra band charactersation have been made for different compounds mostly on the basis of the work of Versaly et al¹² Mounier et al¹³ and Dearbridges on crystalline ZrP.

Infrared spectra of different zirconium based exchangers and tentative band assignments

Table 5.6.1

IR-spectra of ZrAs

Band cm^{-1}	Tentative assignment
3600-3450 (Broad medium)	ν_{OH} (Basic)
~3150 (Medium sharp)	ν_{OH} (Co-ordinated to Zr)
~2350-2250 (very weak, Broad)	ν_{OH} (acidic)
1640 (medium, sharp)	$\delta_{\text{H}_2\text{O}}$ (bending mode of interstitial water)
1250	$\delta_{\text{As-OH}}$
1100	$\nu_{\text{As-O}}$ (as AsO_3)
630	$\delta_{\text{H}_2\text{O}}$
530	$\delta_{\text{As-O}}$ or $\nu_{\text{Zr-O}}$
270	$\nu_{\text{Zr-O}}$

Table 5.6.2

IR-spectra of ZrGAs

Band (cm^{-1})	Tentative assignment
3600-3500 (Broad)	ν_{OH}
~3150	$\nu_{\text{H}^2\text{O}}$
2450	ν_{OH}
2375	ν_{OH}
~1750	ν_{COOH}
1725	
~1675	$\delta_{\text{H}^2\text{O}}$
1600	ν_{COO^-}
1500	ν_{COO^-}
~1400	ν_{AsO}
1150-1000	ν_{AsO}
630	$\nu_{\text{H}^2\text{O}}$
430	$\delta_{\text{As-O}}$ or $\nu_{\text{Zr-O}}$

Table 5.6.3

IR-spectra of ZrAAs

Band (cm^{-1})	Tentative assignment
3600-3500 (Broad)	ν_{OH} (Basic)
~3150	$\nu_{\text{H}^2\text{O}}$
2975 2500	-
~2350	ν_{OH} (acidic)
1750	ν_{COOH}
~1650	$\delta_{\text{H}^2\text{O}}$
1600 1550	$\nu_1 \text{COO}^-$ $\nu_2 \text{COO}^-$
1100 1150	ν_{AsO}
650	$\nu_{\text{H}^2\text{O}}$
420	$\delta_{\text{As-O}}$

Table 5.6.4

IR-spectra of ZrSlAs

Band (cm ⁻¹)	Tentative assignment
3525 3450	ν_{OH} (basic)
~3300	OH coordinated to metal
3175 2375	ν_{H_2O} ν_{OH} (acidic)
~1650 1600	δ_{H_2O} ν_{COO^-}
1550 1525	- OH(probable)
1500	Ph
1475 1425	ν_{COO^-}
1320 1275 1175	M-OH (Probable)
1075 1050	ν_{As-O}
750 650	- ν_{H_2O}

The IR of new compounds have been scanned on the basis of the generalised band data for organic compounds given in literature and also on the basis of comparison to IR of pure organic acids involved in these preparations. Thus tables 5.5.1 to 5.5.4 gives the observed bands (cm^{-1}) and their tentative assignments to characterise the prepared products.

5.5 c Discussion and conclusions

The pure ZrAs prepared by us has shown bands characterising it as amorphous gel. This can be said because in the region from $3600\text{-}3450\text{ cm}^{-1}$ it gives a single broad band instead of three sharp to four sharp peaks (at 3590 , 3510 , 3300 , 3350 cm^{-1} of medium or weak intensities.

The broad band obtained for ZrAs prepared by us is an indication of the disorderly behaviour of gel structure.

Such an structure provides a range of bond energies and hence a broad band in the OH stretch region. This broad band is in between $3600\text{-}3450\text{ cm}^{-1}$ and shows the presence of a hydrogen bonding involving the basic -OH of the polymeric product.

The band at $\sim 3150\text{ cm}^{-1}$ has been characterised as a band due to H_2O co-ordinated to zirconium.

Similarly a band at $\sim 2350\text{ cm}^{-1}$ is for stretching of -OH again but this is the acidic OH attached to Arsenic (ie from H_2AsO_4 part). A band at 1540 cm^{-1} has been shown for the bending mode of the interstitial water molecules.

Later bands at 1250 has been shown for As-OH stretching and 1100 , 1075 , 970 cm^{-1} have been shown for As-O stretching modes. The band 5340 cm^{-1} has been shown for As-O or Zr-O.

All the above peaks have been found in crystalline product with a difference of about $\pm 10 \text{ cm}^{-1}$ in band frequencies.

Now when we compare the obtained characteristic band in ZrGAs, ZrAAs (table 5.5.2 and 5.5.3) with those of Zr-As in all these three new exchangers bands around $\sim 3500 \text{ cm}^{-1}$ or between 3600-3000 have been observed which are quite broad in all the cases signifying the stretching mode of the basic -OH groups in these compounds.

This band is also present in ZrSlAs.

Similarly all contained bands at $\sim 3150 \text{ cm}^{-1}$ unambiguously due to co-ordinated water molecule which is thus common for all compounds including ZrSlAs. The bands at $\sim 2250-2375$ is also similarly common for all the compounds showing stretching mode of the acidic hydroxyl groups.

It is a common understanding in IR-spectral analysis that O-H stretching vibration occur around 3600 cm^{-1} . The formation of hydrogen bond in the region around ~ 3500 are the sure indication of the hydrogen bonding in these compounds.

The presence of water in a sample can be detected by two characteristics bands in the 3600 cm^{-1} to 3000 cm^{-1} region and in the 1650 cm^{-1} region. Similarly presence of lattice water provides bands in 600 to 300 cm^{-1} region. Co-ordination of water also provides a band in 880 to 650 cm^{-1} region depending on these general observations, the presence of a band at 3150 cm^{-1} in all such compounds can be suggested to be due to H_2O molecule. Similarly band at $\sim 1650-1675 \text{ cm}^{-1}$ has been observed in all these compounds and this has been shown by earlier workers on α -ZrP due to the bonding mode of interstitial water. Thus this is

also confirmed mode for water molecules for all the prepared compounds. The presence of a band at $\sim 630-650\text{ cm}^{-1}$ has also been observed in these compounds confirming further the presence of H_2O in these compounds.

This again may be due to the H_2O coordinated to metal atoms.

Thus all these observed bands in ZrGAs, ZrAAs and ZrSlAs confirm the presence of a coordinated molecule of water and probably also an additional water molecule as interstitial H_2O (uncoordinated).

The bands signifying As-O stretching modes are found in all compounds around $\sim 1100\text{ cm}^{-1}$, $\sim 1075-1050\text{ cm}^{-1}$ & at $\sim 530\text{ cm}^{-1}$.

The new compounds possess some additional bands apart from the bands mentioned above which characterise the compounds as zirconium arsenate polymeric net work for these compounds. The new bands present in these compounds are in the region $1750-1700\text{ cm}^{-1}$ which show the presence of $-\text{COOH}$ groups introduced into the above mentioned net work. Similarly two bands have been observed in the region $1600-1550\text{ cm}^{-1}$ and $1475-1325\text{ cm}^{-1}$ region characterising V1 and V2 bands for carboxylate ions. Hence the incorporation of carboxylate part in the compounds is supported by IR spectral data of ZrSAs and ZrAs.

The third compound ZrSlAs has shown additional peaks at $1550, 1525, 1320, 1275$ and 1175 and for $-\text{COO}-$ group band at 1600 cm^{-1} and $1475-1425\text{ cm}^{-1}$ have been also observed.

Thus presence of salicylic acid functional group is justified in this exchanger.

Similarly a peak at $\sim 3300\text{ cm}^{-1}$ is an indicator of $-\text{OH}$

group coordinated to metal atom..

Thus IR-spectral data of the newly prepared compounds thus not only confirms the similarity of the basic net work of these compounds with amorphous ZrP and ZrAs but also proves the involvement of carboxylic acids in their net work structure probably by coordination to the zirconium atom or atoms.

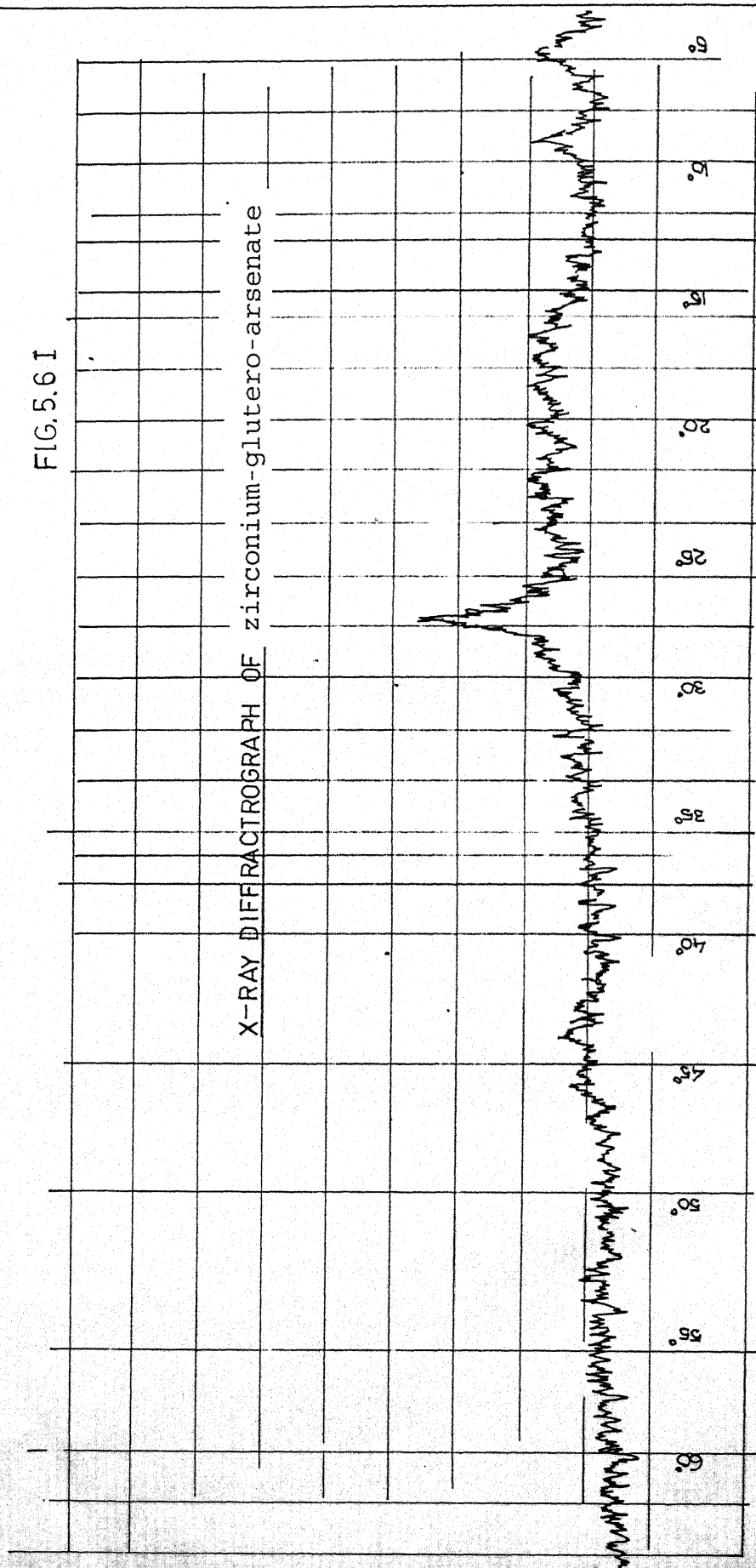
In ZrSlAs coordination of -OH apart from the carboxylic group is also clear from these results. Thus suggestions made in the previous section regarding every of the organic acids in the zirconium arsenate structure by coordination can be supported by these studies.

5.6 X-ray diffraction studies for ZrGAs

As all the new exchangers were prepared under identical conditions. They are expected to show identical crystalline or amorphous characters. Usually the behaviour of crystalline products and amorphous ones show didtinct differences in their x-ray patterns. When a crystalline product can be analysed very clearly by x-ray analysis, an amorphous one simply shows lack of definite x-ray reflections.

Simple ZrAs products have been characterised as monoclinic crystals with unit all dimensions as $a = 9.076 \pm 0.003$ and $b = 5.29 \pm 0.006 \text{ \AA}$ $c = 16.22 \pm 2.02 \text{ \AA}$ while 115.6 ± 0.1 degrees. The values given by Ahrlund et al²⁷ are not very much different from the above. The structure has been shown as a layered one¹¹ as which zirconium atoms lie very nearly in a plane and are bridged by arsenate groups situated alternately above and below the plane of the metal atoms. Any three adjacent metal

FIG. 5.6 I



atoms in the same layer form a slightly distorted equilateral triangle, oxygen atoms of each arsenate group are bounded to the metal atoms.

In the case of amorphous gels the X-ray reflections do not provide an evidence of clear cut crystalline form of any type. However, three or four x-ray reflections are exhibited by such materials^{4,10} which are of a very low intensity.

These reflections appear to occur at roughly the same angles as the stronger reflection in the crystal^{4,10}. The reflections (002) which represents the interlayer spacing in the crystal is very broad and of low intensity and occurs at lower 2 θ angles in gels^{10,8}.

Such a behaviour of x-ray pattern suggests that in gels the inter layer distances are longer than in crystals.

The compound ZrGAs has been exchanged as a representative compound out of the three new compounds by x-ray techniques. It has been examined by the x-rays diffractometer which was a self recording instrument. The radiation used was from a copper target. The gear speed used was 1° per minute.

The x-ray diffractograph obtained for ZrGAs is given in figure 5.6.1 and for comparison purpose a simple ZrAs x-ray diffracts gram has also been obtained under similar conditions (fig. 5.6.II) when these two are examined closely a few x-ray reflections of quite low intensity are clearly perceptible. Thus a sufficiently prominent peak at 27.7° in ZrAs and ZrGAs is noticed.

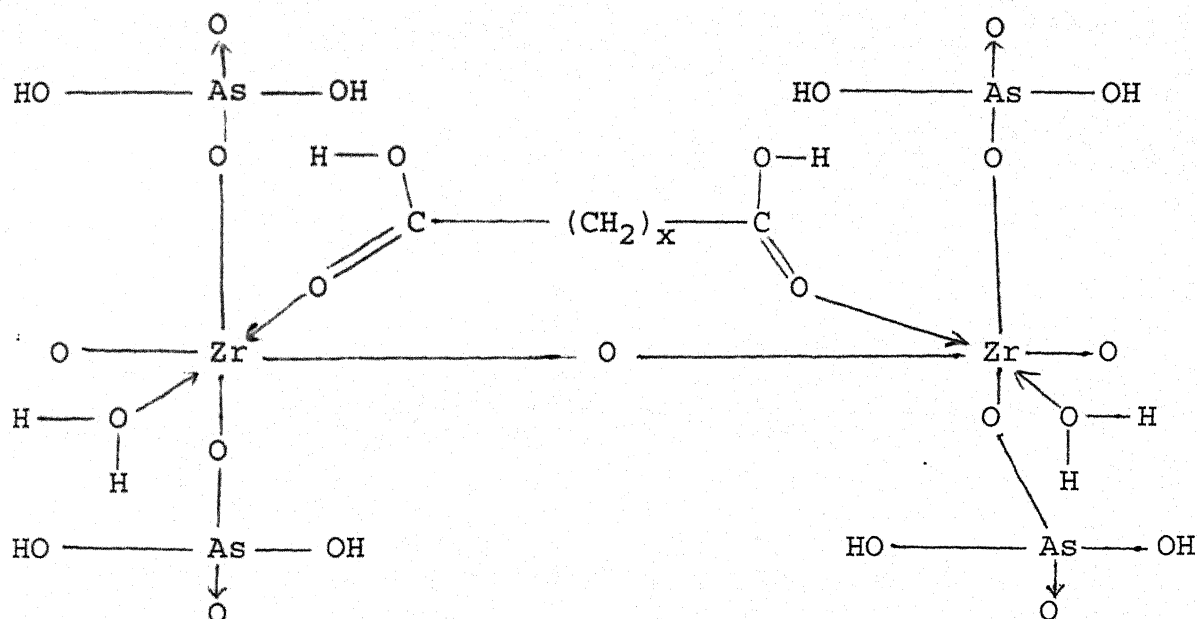
In ZrAs a less prominent peak is found at 9° which is slightly subdivided in ZrGAs at the same angle of reflection on the

lower reflection angle side a broad and a very low intensity peak is also available at $\sim 5^\circ$ in ZrGR₅. The rest of the diffractogram is not showing any distinct x-ray reflection at higher angles particularly.

It is thus clear that ZrGAs like ZrAs is also of amorphous nature. However, this compound shows some x-ray reflections particularly at lower angles of reflection. The reflections are weak and peaks are quite broad at 5° and 9° respectively while one at 27.7° is quite sharp but does not show intense reflection.

If comparisons are made with earlier observations of Clearfield and Stynes⁴ and Stynes¹⁰ then our results for ZrGAs are very close about the nature of the prepared products. The ZrGAs as well as other compounds are definitely amorphous gels. The feeble lower angle intensities reflect in these compounds the broadening of the small crystallinities that might be expected in the amorphous gels. The lower intensities also arise from the disorder which tends to increase the background due to randomly scattered radiations rather than cooperative scattering at specific angles. Hence we also agree with earlier workers like Clearfield et al (loc cit) that the gels are the disordered form of the crystals and it is this thing which causes a random scattering of radiations giving a rather ill defined x-ray diffractogram.

Taking into consideration various views about these compounds and also experimental evidences obtained from IR, x-ray and carbon estimations the tentative structural arrangements in the newly prepared exchangers can be suggested as below for ZrGAs



In such a structure only one water molecule is coordinated to satisfy the 6 coordination possibilities for Zr(IV), the other water molecules in the compound are not termed as compound (or interstitial water molecules) for which 1R has shown an indication. The organic acid involves a claim of a carbon atoms hence a linking involving two zirconium atoms per molecule of the organic acid not unjustified. Similarly structure ZrAP may be explained.

However for ZrSlAs this is not possible as the coordination groups OH-COOH are in adjacent positions in the benzene ring. Hence the linkage is organic molecule per zirconium atoms.

The present studies on this structure determination of the newly formed exchangers are thus quite rewarding in the sense that they provide a good picture of these compounds as far as their compositions is concerned and the presence of extra carboxylic groups is concerned. These structures show that organic acid use their $-C=O$ for coordination to zirconium atoms

and their acidic OH are free to be used for exchange purposes. Thus the new compounds have not the traditional OH groups but also available hydrogen from the acidic -OH of the carboxylic groups. This provides additional exchange capacities to these new compounds. Better exchange capacities ZrGAs, ZrAAs and ZrSlAs are the results of these additional functional groups in these compounds as compared to simple ZrAs without such groups.

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